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Action of Boracic Acid upon Carbonate of Baryta at a dull red heat.

One equivalent (34·9) of boracic acid taken in each case.

No.	Carbonate of baryta in equivalents (1 eq. = 98·5).	Carbonic acid expelled in equivalents.
62	2·82	1·96
63	3·00	2·15
64	3·65	1·92
Mean of 3 experiments		2·01

In No. 63, the hydrated boracic acid dried at 212° was employed; in the other cases crystallised acid was taken.

At a dull red heat, boracic acid expels 2 eqs. of carbonic acid from the carbonate of baryta.

At a bright red heat.

No.	Carbonate of baryta in equivalents.	Carbonic acid expelled in equivalents.
65	2·82	2·56 ($3HO.BO_3$)
66	2·87	2·42 (BO_3)
67	2·94	2·56 (BO_3)
68	3·00	2·60 ($HO.BO_3$)
69	3·01	2·45 (BO_3)
70	3·04	2·44 (BO_3)
71	3·22	2·47 (BO_3)
72	3·50	2·56 ($3HO.BO_3$)
73	3·65	2·70 ($3HO.BO_3$)
Mean of 9 experiments		2·53

The fused masses obtained here had many of the properties of caustic baryta, becoming heated when moistened with water, which partially dissolved them, yielding powerfully alkaline solutions, which deposited carbonate of baryta when exposed to the air.

In the experiments with carbonate of baryta it was remarkably easy to obtain a constant weight, but I found that no advantage could be taken of this in the valuation of commercial boracic acid, since the ammonia and other volatile matters favour the escape of a larger quantity of carbonic acid.

It appears, therefore, that boracic acid expels $2\frac{1}{2}$ eqs. of carbonic acid, both from carbonate of baryta and from carbonate of lithia at a bright red heat.

Action of Boracic Acid upon Carbonate of Strontia at a dull red heat.

One equivalent (34·9) of boracic acid taken in each case.

No.	Carbonate of strontia in equivalents (1 eq. = 73·8.)		Carbonic acid expelled in equivalents.	
74	3·67	min.	2·37	($3HO.BO_3$)
75	3·76	.	2·52	($HO.BO_3$)
76	4·78	.	2·61	„
77	6·65	.	2·40	($3HO.BO_3$)
78	9·00	.	2·62	„
Mean of 5 experiments		max.	2·50	

At a dull red heat, then, hydrated boracic acid expels $2\frac{1}{2}$ eqs. of carbonic acid from the carbonate of strontia.

In consequence, apparently, of the difficulty of fusing the borate of strontia, it was found that no uniform results could be obtained by igniting fragments of glassy boracic acid with precipitated carbonate of strontia; it was necessary to employ the boracic acid in the hydrated state, and to mix thoroughly with a glass rod, afterwards drying at a gentle heat before igniting over the gas-furnace.

At a bright red heat.

No.	Carbonate of strontia in equivalents.		Carbonic acid expelled in equivalents.
79	3·67	.	2·90
80	3·76	.	2·92
81	3·76	.	3·03
82	4·78	min.	2·86
83	6·65	max.	3·18
84	9·00	.	3·14
Mean of 6 experiments		.	3·00

It was rather more difficult to obtain a constant weight in the case of carbonate of strontia than in that of carbonate of baryta.

It may be remarked that there is just half an equivalent more carbonic acid expelled from each of these last carbonates at a bright red, as at a dull red heat.

From the experiments above recorded, I should infer (though the results in the case of soda at a bright red heat are somewhat doubtful) that the quantities of carbonic acid expelled by boracic acid at a dull red heat, from the carbonates of soda, lithia, baryta, and strontia respectively, are approximately in the ratio of the numbers 1, $2\frac{1}{2}$, 2, and $2\frac{1}{2}$, and that the quantities of carbonic acid expelled, at a bright red heat, from the carbonates of potassa, soda, lithia, baryta, and strontia, respectively, are approximately as the numbers 1, 2, $2\frac{1}{2}$, and 3.

What explanation can be given of these results? It can hardly be supposed that there are four different equivalent weights to be assigned to boracic acid, as representing the quantities required to displace a given amount of carbonic acid from its combinations with these different bases.

It appears far more reasonable, and far more in harmony with our knowledge of the chemical relations existing between these bases, and more particularly of their relations to carbonic acid, to attribute the progressive increase in the quantity of carbonic acid evolved to a corresponding decrease in the chemical attraction for that acid evinced by the several bases in question.

In each case the decomposition may be supposed to proceed until the tendency of the borate which has been found to take up an additional quantity of base is in a state of equilibrium with the chemical attraction existing between that base and the carbonic acid.

Thus, in the case of carbonate of potassa, the monoborate of potassa ($KO.BO_3$) which is formed at a bright red heat, has only just so much attraction for an additional quantity of potassa as is counteracted by the opposing attraction of the potassa for the carbonic acid, whilst, in the case of carbonate of strontia, the attraction between that base and the carbonic acid is only sufficient to counteract the tendency of the compound $3SrO.BO_3$ to take up an additional quantity of strontia.

If this were the true explanation, it might be expected that boracic acid, which had already been fused with an excess of carbonate of potassa, would still be able to expel carbonic acid from carbonate of soda, or of lithia; for, allowing the $KO{\cdot}BO_3$ a certain attraction for an additional amount of base, it will be

capable of satisfying that attraction if the base presented to it have a weaker attraction for carbonic acid than the potassa has.

(85). 15·3 grns. of glassy boracic acid were fused over the gas-blowpipe, with 37·7 grns. (1·246 eq. for each eq. of BO_3) of fused carbonate of potassa for fifteen minutes, weighed, and again ignited for five minutes, when a further loss of only 0·02 grn. had occurred.

The carbonic acid expelled amounted to 10·39 grns, or 1·07 eq. for each eq. of BO_3. 14·05 grns. of pure fused carbonate of soda (0·60 eq. for 1 eq. BO_3) were then added, and the crucible again heated for ten minutes over the gas-blowpipe, weighed (loss= 1·98 grns.), again heated for five minutes, causing a further loss of 0·28 grn., then a gain for five minutes, when it lost only 0·1 grn.

The carbonic acid expelled from the carbonate of soda by the boracic acid, which had been already saturated with carbonate of potassa, amounted to 2·20 grns., or 0·227 eq. for each eq. of BO_3 present.

(86). A similar experiment with
7·12 grns. glassy boracic acid (1 eq.) and
18·14 grns. fused carbonate of potassa (1·28 eq.)
Final variation after five minutes ignition, 0·02 grn.
Carbonic acid expelled from the carbonate of potassa, 4·86 grns., or 1·08 eq.
17·40 grns. (1·60 eq.) of carbonate of soda added.
Loss in fifteen minutes' ignition, 2·07 grns.
Final variation after five minutes' ignition, 0·04 grn.
Carbonic acid expelled from the carbonate of soda by the boracic acid already saturated with carbonate of potassa amounted to 2·11 grns., or 0·47 eq. for each eq. of BO_3.

(87). 8·72 grns. glassy boracic acid (1 eq.)
42·52 grns. fused carbonate of potassa (2·46 eqs.)
Final variation in five minutes' ignition, 0·1 grn.
12·04 grns. more carbonate of potassa added.
Further loss after fifteen minutes' ignition, 0·32. grn.
Carbonic acid expelled from the carbonate of potassa, 1·30 eq
17·48 grns. (1·32 eq.) of fused carbonate of soda added.
Loss in six minutes' ignition, 0·64 grn.
Final variation in five minutes' ignition, 0·12 grn.

Carbonic acid expelled from the carbonate of soda by the boracic acid already saturated with carbonate of potassa amounted to 1·16 grn., or 0·21 eq. for each eq. BO_3.

(88.) 14·09 grns. of glassy boracic acid (1 eq.)
47·53 grns fused carbonate of potassa (1·61 eq.)
Final variation after five minutes' ignition, 0·03 grn.
6·97 grns. more carbonate of potassa added.
Further loss after ten minutes' ignition, 0·27 grn.
Final variation after five minutes' ignition, 0·00.
Carbonic acid expelled from the carbonate of potassa, 1·14 eq.
9·43 grns. (0·42 eq.) of fixed carbonate of soda added.
Loss in five minutes' ignition, 0·65 grn.
Final variation in five minutes' ignition, 0·08 grn.

Carbonic acid expelled from the carbonate of soda by boracic acid already saturated with carbonate of potassa, 1·44 grns., or 0·15 eq. for each eq. BO_3.

(89.) 10·02 grns. of glassy boracic acid (1 eq.)
63·78 grns. of fused carbonate of potassa (3·2 eqs.)
Final variation after five minutes' igniton, 0·05 grn.
6·58 grns. more carbonate of potassa added.
Further loss after five minutes' ignition, 0·04 grn.
Carbonic acid expelled from the carbonate of potassa, 1·21 eqs.
11·57 grns. (0·76 eq.) of fused carbonate of soda added.
Loss in five minutes' ignition, 0·53 grn.
Final variation in five minutes' ignition, 0·12 grn.
5·98 grns. more carbonate of soda added.
Further loss in five minutes' ignition, 0·24 grn.
Added 3·03 grns. more carbonate of soda.
Further loss in five minutes' ignition, 0·28 grn.
Final variation, 0·10 grn.
Added 4·57 grns. more carbonate of soda.
Final variation in five minutes' ignition, 0·17 grn.

Carbonic acid expelled from the carbonate of soda by boracic acid already saturated with carbonate of potassa, 1·84 grns., or 0·29 eq. for each eq. of boracic acid.

Added 2·75 grns. (0·26 eq.) of carbonate of lithia.

Loss in five minutes' ignition, 0·51 grn.
Final variation 0·12 grn.

Total loss after adding the carbonate of lithia	1·15	grn.
Deduct the maximum loss ever suffered by carbonate of lithia heated alone (15 per cent.)	0·41	„
Carbonic acid expelled	0·74	(0·11 eq.)

from the carbonate of lithia by boracic acid already saturated with carbonate of potassa and carbonate of soda.

(90.) 8·09 grns. glassy boracic acid (1 eq.)
64·86 grns. fused carbonate of potassa (3·6 eqs.)
Final variation after seven minutes' ignition, 0·12 grn.
13·05 grns. more carbonate of potassa added.
Further loss after five minutes' ignition, 0·07 grn.
Carbonic acid expelled from the carbonate of potassa, 1·26 eqs.
Added 6·47 grns. (0·69 eq.) of carbonate of lithia.
Loss in five minutes' ignition 1·33 grns.
Final variation 0·13 grn.

Total loss after adding the carbonate of lithia	2·24	grns.
Deduct the maximum loss ever suffered by carbonate of lithia alone	0·97	„
Carbonic acid expelled	1·27	(0·136 eq.)

from the carbonate of lithia by boracic acid already saturated with carbonate of posassa.

(91.) 9·93 grns. glassy boraric acid (1 eq.)
81·42 grns. fused carbonate of soda (5·4 eqs.)
Final variation after five minutes' ignition, 0·08 grn.
12·75 grns. more carbonate of soda added.
Further loss in five minutes' ignition, 0·08 grn.
Carbonic acid expelled from the carbonate of soda, 2·31 eqs.
Added 4·46 grns. carbonate of lithia (0·42 eq.)
Loss in five minutes' ignition, 0·46 grn.
Final variation, 0·17 grn.

Total loss after adding carbonate of lithia .	1·00 grn.
Deduct maximum loss of carbonate of lithia alone	0·67 „
Carbonic acid expelled	0·33 (·031 eq,)

from the carbonate of lithia by boracic acid already saturated with carbonate of soda.

We are not surprised that the amount of carbonic acid expelled is in this case so small when we remember that 2·5 eqs. represent the average amount of carbonic acid expelled from carbonate of lithia by boracic acid, and that as much as 2·31 eqs. were here expelled from the cabonate of soda alone before any carbonate of lithia was added.

It still remained to be seen whether boracic acid which had been saturated with carbonate of soda was not capable of expelling carbonic acid from carbonate of potassa.

(92.) 14·14 grns. glassy boracic acid (1 eq.)
43·25 grns. fused carbonate of soda (2·01 eqs.)
Final variation after five minutes' ignition, 0·05 grn.
Carbonic acid expelled from the carbonate of soda, 1·79 eqs.
Added 31·51 grns. of fused carbonate of potassa.

Instead of suffering any further loss, the mass now actually *gained* 0·05 grn. in five minutes' ignition; it was then heated for ten minutes, when it had gained 0·07 grn. in addition, and on again heating for five minutes, it had still gained 0·05 grn.

This result is the more satisfactory because the boracic acid had not expelled from the carbonate of soda the greatest amount of carbonic acid which it is capable of displacing, and still it refused to expel any carbonic acid from the carbonate of potassa.

(93.) 16·04 grns. glassy boracic acid (1 eq.)
55·51 grns. fused carbonate of soda (2·4 eqs.)
Final variation after five minutes' ignition, 0·09 grn.
Carbonic acid expelled from carbonate of soda, 1·86 eqs.
Added 21·3 grns. fused carbonate of potassa.
Further loss in fifteen minutes' ignition, 0·2 grn.

It is evident, therefore, that boracic acid which has been saturated

with carbonate of soda has no longer any tendency to expel carbonic acid from carbonate of potassa.

It appeared probable that silicic acid would be found to behave with the two alkaline carbonates in the same manner as boracic acid.

(94.) 9·52 grns. (1 eq.*) of precipitated silicic acid were fused over the gas-blowpipe with 46·75 grns. (2·15 eqs.) of fused carbonate of potassa till a loss of only 0·04 grn. was observed after five minutes' ignition: the crucible was then placed for ten minutes in a very hot muffle, when it only lost 0·13 grn. The carbonic acid expelled amounted to 6·63 grns., or 0·95 equivalent for each equivalent of silicic acid.

(95.) 9·84 grns. (1 eq.) of silicic acid.
57·80 grns. (2·57 eqs.) fused carbonate of potassa.
Final variation after five minutes' ignition, 0·06. grn.
Carbonic acid expelled, 6·68 grns., or 0·93 eq.
Added 29·17 grns. fused carbonate of soda.
Loss in five minutes' ignition, 0·79 grn.

Total loss after eighteen minutes, 1·21 grn. (0·17 eq.) of carbonic acid expelled from carbonate of soda by silicic acid already saturated with carbonate of potassa.

(96.) 10·57 grns. (1 eq.) of finely powdered rock crystal, fused with 66·83 grns. (2·77 eqs.) of fused carbonate of potassa.
Final variation in five minutes' ignition, 0·05 grn.
Carbonic acid expelled, 6·96 grns. (0·9 eq.)
Added 18·86 grns. fused carbonate of soda.
Loss in five minutes' ignition, 0·28 grn.

Total carbonic acid, 0·55 grn. (0·07 eq.) expelled by the silicic acid already saturated with carbonate of potassa.

(97.) 9·68 grns. (1 eq.) precipitated silica, and
34·60 grns. (2·03 eqs.) pure carbonate of soda, intimately mixed.

Heated to dull redness till nearly constant in weight, had lost 4·87 grns. (0·69 eq.) of carbonic acid.

* The equivalent weight of silicic acid is here taken a 30·24 (SiO_2).

Heated for fifteen minutes over gas-blowpipe, had lost 9·09 grns. (1·30 eq.)

Heated for ten minutes in hot muffle, had lost 9·79 grns. (1·39 eq.)

(98.) 9·31 grns. (1 eq.) precipitated silica.
34·06 grns. (2·12 eqs.) carbonate of soda
Heated over gas-blowpipe till nearly constant, had lost 9·24 grns. (1·36 eq.) of carbonic acid.

(99.) 10·4 grns. (1 eq.) precipitated silica.
35·34 grns. (1·93 eq.) fused carbonate of soda.
Final variation in five minutes' ignition. 0·03 grn.
Carbonic acid expelled, 9·92 grns. (1·31 eq.)
Added 47·16 grns., fused carbonate of potassa, and again fused.
After five minutes' fusion, the mass had actually *gained* 0·1 grn.

(100.) 6·89 grns. (1 eq.) of rock crystal.
45·93 (2·6 eqs.) fused carbonate of soda.
Final variation in five minutes' ignition, 0·1 grn.
Carbonic acid expelled, 9·68 grns. (1·34 eq.)
Added 15·28 grns. fused carbonate of potassa, and again fused.
Gain in five minutes' ignition, 0·17 grn.
" in other five minutes, 0·08 „
Final variation in five minutes, 0·00 „

It is evident from these results that no carbonic acid can be expelled from carbonate of potassa by silicic acid already saturated with carbonate of soda.

The conclusion deducible from these few experiments upon the action of silicic acid on the alkaline carbonates, at high temperatures, agrees pretty well with that furnished by the experiments of Col. Yorke, who found that 1 eq. (30·24) of silicic acid expelled 0·97 eq. of carbonic acid from carbonate of potassa, and 1·42 eq. from carbonate of soda. I found 0·926 expelled from carbonate of potassa, and 1·35 from carbonate of soda.

It was also much easier to obtain a constant weight with carbonate of potassa, and the results exhibited less variation.

Further experiments upon the expulsion of other acids from their salts by boracic and silicic acids appear to be required before we can safely infer that the attraction of boracic acid

for bases, at high temperatures, is really greater than that of silicic acid.

It would appear that in all attempts to determine the equivalent of an acid by the amount of carbonic acid displaced by it at high temperatures, it would be safer to employ carbonate of potassa than carbonate of soda, since the latter, in the case of the two acids here examined, has yielded far less constant results.

On comparing the action of boracic acid upon carbonate of potassa at a bright red heat with that of silicic acid, I am led to the belief that if the equivalent of the former acid be taken as = 34·9 (BO_3), then the equivalent of silicic acid must be that which corresponds to the formula SiO_2.

XX.—*On the Colouring Matters of Madder.*

By Edward Schunck. Ph.D., F.R.S., F.C.S.

The root of the *Rubia tinctorum*, commonly called madder, constitutes one of the most valuable dyeing materials employed in the arts. Though probably known to the ancients, it is only in modern times that it has come to be extensively used. At the present time, there is, perhaps, no dye-stuff, with the exception of indigo, employed to so great an extent in imparting various colours to calico and other fabrics as madder; and a knowledge of its properties and the most advantageous mode of treating it is indispensable to any one engaged in the arts of dyeing and printing. It stands in about the same relation to other dye-stuffs, in the eyes of the dyer and calico-printer, as iron does to other metals in the eyes of the engineer.

The principal advantages which madder presents are the following:—1. It is capable of producing, according to the mordants employed and the method of treatment, a great variety of different colours and shades, such as black, red of different kinds from a dull brownish-red to a bright red and a delicate pink, besides the peculiar colour of Turkey red, also purple of various shades from a dull reddish-purple to a delicate bluish-purple or lilac, as well as cho-

colate of all shades.—2. Its colouring matters have but little affinity for cotton fibre and a great affinity for mordants, so that it is not difficult to secure a good white on the parts of the tissue to which no mordant has been applied.—3. The compounds which its colouring matter or matters yield with mordants possess an unusually stable character, so that it is possible, without causing much detriment to the colour, to expose them to the action of various agents for the purpose of improving or modifying the shade. They are also capable of resisting the action of air and light in a remarkable degree, so much so that I am inclined to believe that the fading which we observe in colours produced by madder is caused rather by the mechanical wear and tear of the fabric than by any chemical decomposition of the colours themselves. It is these properties, chiefly, which have led to the extensive employment of madder in the arts of dyeing and calico printing.

The art of employing madder to the greatest advantage had, like many other arts, attained to a considerable degree of perfection, before any attempt was made to elucidate the principles involved in it. Indeed the art of Turkey-red dyeing affords a striking instance of a very complicated process of manufacture arriving at a state of great perfection, without one step in the process being really understood and without the least improvement having been made in it by any one conversant with the principles of chemical science. All processes in which the action of colouring matters are concerned, are in fact of so complicated a nature, and depend on the action of bodies for the most part so remote from the ordinary experience of the chemist, that their elucidation could only be attempted when the science had attained a high degree of developement. The process of fermentation, for instance, which plays a considerable part in the formation of many colouring matters, is one that could not possibly be understood in the early ages of the science of chemistry. All that could be accomplished was to describe the processes actually in use in the arts, without any successful attempt at their explanation. Chevreul, whose interesting and important labours on colouring matters are so well known, seems not to have occupied himself with any chemical examination of madder. The first discovery of any importance in this branch of chemistry was made by Robiquet and Colin, who succeeded in preparing from madder a substance, which on being exposed to heat gave a sublimate consisting of beautiful reddish-yellow needles, and to which they gave the name of *Alizarine*.

This substance they found to be very little soluble in water, but soluble in alcohol and ether. Its alkaline solutions were of a beautiful violet or purple colour, and it gave with earths and metallic oxides lakes of various colours. The method of preparation which they adopted, left it quite uncertain whether alizarine pre-existed in madder or whether it was a product of decomposition of some other body formed by the action of heat. It is only by recent researches that its pre-existence in the ordinary madder of commerce has been established. But finding that all the usual madder colours could be produced by its means, and moreover of great brilliancy and purity, Robiquet and Colin were right in attaching to it a considerable degree of importance. The same series of experiments led to the discovery of another colouring matter in madder, to which these chemists gave the name of *Purpurine*. This they found to be distinguished from the preceding chiefly by being soluble in alum-liquor, the solution having a beautiful pink colour. In other respects it did not differ very much from alizarine. It yielded a crystalline sublimate when heated; it was very sparingly soluble in water, but more soluble in alcohol, and its alkaline solutions were reddish-purple.

The red and pink colouring matters of madder obtained by Gaultier de Claubry and Persoz are, as Persoz himself confesses, identical with the alizarine and purpurine of Robiquet and Colin. To the former chemists however clearly belongs the merit of a very important discovery in the chemistry of madder, viz., that of the effect produced on madder by strong mineral acids. They found that when madder was treated with boiling dilute sulphuric acid, it was converted into a dark brown powder, which could afterwards be completely washed with cold water without any of the colouring matters being removed, the latter remaining in the residue, while many impurities were washed away by the water. The residue was found to yield in dyeing better results, in some respects, than madder itself, the colours being more brilliant and requiring very little after-treatment, while the white portions of the fabric remained unsullied. This process has since then been carried out on a large scale, the product having obtained the name of *Garancine*. This was the first instance that had occurred of the labours of the scientific chemist having been applied to the improvement of the art of madder-dyeing. Persoz as well as Robiquet, explained the action of the acid on madder by supposing that the saccharine, gummy and extractive matters contained in the root and pre-

sumed to be injurious during the process of dyeing, were charred or otherwise decomposed by the acid, or afterwards removed during the washing, the undecomposed colouring matters being left behind in a state of greater purity. This explanation, though it had at the time every appearance of probability, was afterwards discovered to be only partially correct, the acid having been found to produce other effects in addition to this.

Besides these two colouring matters, another was discovered in madder by Kuhlmann and called by him *Xanthine*. It was described by him as a substance resembling extractive matter, having a taste between bitter and sweet, and a yellow colour, being very easily soluble in water, and giving rise by the action of strong acids to the formation of a dark green powder.

About the year 1835, a memoir was published by Runge, containing a description of the properties and method of preparation of three distinct colouring matters from madder, which he named respectively *Madder-red, Madder-purple,* and *Madder-orange*. There can be no doubt that the two first are identical with the alizarine and purpurine of Robiquet. The discovery of madder-orange was the first indication of the existence of crystallized yellow colouring matters in madder. The memoir of Runge, which contained also an account of other substances not of any importance, as far as the process of dyeing was concerned, was for a number of years referred to as an authority on the subject, and for a long time no facts of any great importance were added to those previously known.

This short account may serve to give an idea of the state of our knowledge on this subject at the time when I entered on its investigation. My efforts were in the first place directed to the separation, as far as possible, of all the substances contained in the ordinary madder of commerce from one another, their preparation in a state of purity, and their mutual action and reaction during the process of dyeing. After much labour I succeeded in obtaining Robiquet's alizarine in a well crystallized state without having recourse to sublimation. The alizarine thus obtained differed from sublimed alizarine in containing several atoms of water of crystallization, which were lost even on heating the crystals to 100°C. Its colour inclined also more to yellow and had less of the reddish tinge seen in sublimed alizarine. Hence it followed that ordinary madder, in the state in which it is employed by the dyer, does in reality contain ready formed alizarine, and that the latter

is not a product of decomposition formed from some other substance by heat. My experiments regarding the tinctorial power of alizarine, which have often been repeated since then, fully confirmed those of Robiquet. I found that, by means of alizarine, I could produce all the usual madder colours, and moreover that the colours so produced were distinguished for their brilliancy and purity, being as beautiful as the ordinary madder colours, after they have been subjected to a long course of treatment with soap, acids &c., for the purpose of rendering them more brilliant. This simple fact, like many others connected with the chemistry of madder, has been the subject of much controversy. It has been asserted by D. Köchlin that alizarine is not strictly speaking a colouring matter, but a mixture of a colourless crystallised resin with a red colouring matter, and that it owes to the latter its tinctorial power. That this view is entirely erroneous must be obvious to any person possessing any knowledge of chemistry, who has occupied himself with this subject. Its unvarying properties and the uniformity of its composition prove alizarine to be a pure unmixed substance. That it plays a principal, if not the only part, in the production of the colours for which madder is employed, seems probable from the circumstance that the finer madder colours contain little besides alizarine in combination with the mordants. If, for instance, a few yards of so-called madder-pink calico be treated with muriatic acid to remove the alumina of the mordant, then well washed and treated with caustic alkali, a violet-coloured solution is obtained from which acids precipitate yellow flocks, consisting of almost pure alizarine, which may be obtained in long crystalline needles by solution in boiling alcohol and evaporation of the alcoholic solution. This constitutes, indeed, the easiest method of preparing pure alizarine on a small scale. The colours produced by pure alizarine do not yield to ordinary madder colours in their power of resisting decomposition by alkalies, soap, &c., they are equally fast, as was observed long since by Robiquet and others. I have, in fact, after a long course of experiments, been led to the conclusion, that the final result of dyeing with madder and its preparations is simply the combination of alizarine with the various mordants employed, and that consequently if an economical method of preparing alizarine on a large scale could be discovered, a great gain would result to the arts.

The analyses of pure alizarine made by myself and others have led to pretty nearly the same elementary composition. The formula

which I gave to it in the first instance, viz. $C_{14}H_5O_4$ or $C_{28}H_{10}O_8$, I have never seen any cause to deviate from. Indeed all my subsequent researches have appeared to me only to confirm it. It is at all events certain that, the purer the alizarine, the more nearly does its composition approach what it should be according to this formula. By the action of nitric acid, alizarine is converted into a colourless beautifully crystallised acid, which subsequent investigations have proved not to be new, as I at first supposed, but identical with phthalic acid, one of the many products of decomposition of naphthaline discovered by Laurent. From this fact, conclusions have been drawn regarding the composition of alizarine, which I cannot but consider as erroneous. Since chloronaphthalic acid and alizarine both yield phthalic acid by decomposition with nitric acid, Strecker has inferred that there must be a similarity in the composition of the two bodies, that the formula of alizarine is $C_{20}H_6O_6$, and that consequently chloronaphthalic acid is simply alizarine with 1 At. of hydrogen replaced by chlorine; and he has adduced many ingenious arguments in favour of this view. If this view of the composition of alizarine were correct, it would lead to very important conclusions, as the possibility of converting a refuse product like naphthaline, into one of great value and importance would in that case not be so very remote. The attempts made by Strecker to replace the atom of chlorine in chloronaphthalic acid by hydrogen and thus convert it into alizarine did not succeed. The far easier experiment of converting alizarine into chloronaphthalic acid by the action of chlorine he does not seem to have attempted. In order to complete the presumed analogy between chloronaphthalic acid and alizarine, Strecker supposes the latter, like the former, to yield oxalic acid as well as phthalic acid by decomposition with nitric acid. This is however not the case, as no trace of oxalic acid is formed from alizarine by oxidising agents.

By a process similar to that adopted by Runge for the preparation of his madder-orange, I succeeded in obtaining a body crystallising in beautiful golden yellow needles and scales, to which I gave the name of *Rubiacine*. This was the first to be discovered of a series of yellow colouring matters from madder, having very similar properties and a similar composition. These colouring matters are all capable of crystallising, and though yellow themselves, yield red compounds with bases. They do not contribute to the production of fast colours during the process of madder dyeing,

but are, on the contrary, as my experiments show, very injurious to the strength and beauty of those colours. The most characteristic property of rubiacine is the facility with which it is converted by the action of persalts of iron into a new acid, *rubiacic acid*, which yields definite crystallised compounds with alkalies. By means of these compounds, it was possible to determine the composition and formula of the acid with a tolerable degree of certainty; and as the acid was again convertible into rubiacine by the action of sulphuretted hydrogen, it followed that the number of equivalents of carbon in both bodies must be the same. This number I found to be 32. In what relation, however, the composition of rubiacine stood to that of alizarine was at first not all apparent, as the link uniting the two bodies had still to be discovered. According to the old classification of colouring matters, rubiacine would belong to the division called resinous, from being insoluble in water, but soluble in alkaline liquids and alcohol, and from its power of resisting the action of strong reagents such as nitric and sulphuric acids. It is a remarkable fact that rubiacine is oxidised and converted into rubiacic acid by means of persalts of iron, whereas the same change is not produced by nitric acid. It is improbable that this difference is owing to any predisposing affinity of the peroxide of iron for rubiacic acid, though there is no doubt that some combination does take place; for on treating rubiacine with boiling solutions of persalts of iron, it dissolves with a dark brownish-red colour, and the solution, after being boiled for some time, contains rubiacic acid, which is precipitated in yellow flocks on the addition of muriatic or nitric acid, the solution itself becoming yellow.

Two other bodies still more nearly resembling resins, yielding red compounds with bases, but not themselves capable of crystallising, were discovered in madder. These I found to be equally injurious with rubiacine in the process of dyeing. It is only a consideration of the source whence they are derived which lends to these bodies the least interest.

For the purpose of completely understanding all the phenomena which take place during the process of madder dyeing, I considered it necessary to ascertain what other constituents the root contains besides colouring matters. Several of these, such as sugar and pectic acid, have for a long time been known as constituents of madder. The latter may under certain circumstances act very injuriously in dyeing. The xanthine of Kuhlmann is a mixed

substance. It contains a body which by the action of strong acids becomes dark green, and yields a green powder. It is this body, to which I have given the name of *Chlorogenine*, and which Rochleder calls *Rubichloric Acid*. It is a species of extractive matter. Its watery solution, when heated and exposed to the air, acquires a brown colour, and in this state is capable of imparting a brown tinge to calico, whether mordanted or unmordanted. Hence the uniform dirty reddish-brown tint which a piece of calico exhibits both on the printed and unprinted portions, after having been dyed with madder; to remove this tinge is one of the objects of the after treatment with soap and other materials. In the process of manufacturing garancine, this substance is partly decomposed, partly removed by the subsequent washing. Hence may, in a great measure, the greater purity and brilliancy of gerancine colours, as compared with madder colours, be explained.

There is a point connected with the chemistry of madder dyeing which has puzzled many, especially practical, persons who have devoted their attention to the subject, that is the apparent necessity of having a certain proportion of lime or its carbonate, either mixed with the material. or contained in the water of the dye-bath, in order to produce colours which shall resist the subsequent action of soap and other agents. It is a fact well known, since the time of Hausmann, that in order to insure fastness of colour, it is necessary, either to employ calcareous water or to add chalk to the dye-bath, the effect of so doing being to impoverish the colours, but at the same time to add to their permanency. Hence, too, madder grown in a calcareous soil is superior to any other, and for some colours dyers generally make up for a deficiency of lime in the root by the addition of chalk. Now the experiments of Robiquet, as well as my own, have demonstrated that in dyeing with pure alizarine, the least addition of lime is rather injurious than otherwise, as it merely weakens the colours without adding to their durability. Hence the beneficial effect of lime can only be accounted for by some action which it exerts on other constituents of the root. Now I found that the addition of rubiacine, or of any of the resinous colouring matters to alizarine, during the dyeing produced very prejudical effects. They weakened the colours and rendered them impure and unsightly. The red acquired an orange, the purple a reddish hue, while the black became brownish, and the white parts assumed a yellowish tinge. These effects disappeared, however, completely, as soon as the foreign colouring

matter was completely saturated with lime, the tinctorial power of the alizarine then appearing again with all its original intensity, while the other colouring matter was rendered innocuous. The same prejudicial effect was produced by adding free pectic acid to the alizarine, but disappeared entirely on neutralising the pectic acid with lime. The phenomenon seems, therefore, to resolve itself into a simple case of elective affinity. The resinous colouring matters and other bodies having a stronger affinity for bases than alizarine, seize hold of the alumina and other mordants when all are uncombined, but when lime is added, they combine with it as the stronger base, leaving the alizarine at liberty to unite with the mordants. At the same time, I do not suppose, even if a specimen of madder contain exactly sufficient lime to unite with the resinous colouring matters, pectic acid and other injurious substances existing in it, that the distribution of these substances and the alizarine among the bases will be precisely as my theory presupposes; for if even in a mixed solution containing various salts of strong mineral acids and bases, it still remains a subject of speculation with chemists, in what manner the acids and bases are mutually distributed, and whether every base is not combined with every acid, how much less can we expect it to be a settled matter according to what law a certain number of complex organic bodies existing in solution together will distribute themselves among a certain number of bases. In the case just mentioned I believe, on the contrary, that however large an excess of lime or other base be taken, a certain quantity only of the resinous colouring matters, &c., will combine with the lime or other base, while the remainder will go to the mordants and can only be separated by after-treatment, a small portion of the alizarine at the same time uniting with the lime or other base, and a larger portion with the mordants. Indeed this view of the case may be proved to be correct; for if a piece of printed calico be dyed in the usual manner with madder to which chalk has been added, the colour is found on examination to contain, in combination with the mordants, not only alizarine, but also a small quantity of resinous colouring matter as well as pectic acid, and a brown substance insoluble in alcohol, which I suppose to be a product derived by oxidation from xanthine or chlorogenine. These impurities are subsequently removed by means of soap, acids, &c., leaving a compound containing only alizarine and a little fatty acid on the fabric. Now the residual madder left after the dyeing is com-

pleted, though apparently exhausted of colouring matter, may be proved to contain alizarine; for if it be treated with acids, a quantity of lime, magnesia, &c., is removed, and after being washed it is found to be capable of dyeing anew, and a fresh portion of alizarine and other substances may now be extracted by means of caustic alkalies. On this depends the manufacture of so-called *garanceux* from the waste madder of dye-houses, a product which used formerly to be thrown away.

When fresh madder is subjected to the action of strong acids for the purpose of manufacturing *garancine*, the following effects take place: 1. The sugar, xanthine, and other injurious substances soluble in water are either washed away or decomposed by the acid and so removed. 2. The lime, magnesia, and other bases which would prevent the colouring matter from exerting its full effect are removed, and thus, after the washing is completed, a suitable quantity of lime, soda or some base is added in order to combine with and render innocuous the resinous colouring matters, as well as the pectic acid, which, as is well known, is capable of taking up a certain quantity of mineral acids, forming with them compounds not easily soluble in water. There is another effect produced by the acid, in addition to those just named, which I shall refer to presently. To the view here taken it may be objected, in the first place, that the fact of the colours produced by alizarine being more durable and resisting better the action of alkalies, &c., than the compounds of the other colouring matters of madder with mordants, is inconsistent with the supposition of its having less affinity for bases than the other colouring matters. Secondly, that ordinary garancine, even when a sufficient quantity of base has been added to it to combine with the impurities which prevent the alizarine from uniting with the mordants, does not in practice produce exactly the same effect as madder. Garancine colours are notoriously not as fast as madder colours, and hence garancine cannot be made to replace madder completely, however great its advantages are in other respects. To the first objection it is certainly difficult to frame a convincing reply. The second will fall to the ground at once, when I state that, by a very simple process, garancine may be so modified as to be capable of affording colours as permanent as those from madder itself—nay, even more so. This process, which was patented by Mr. Pincoffs and myself several years ago, consists simply in subjecting garancine to the action of high pressure steam, or in heating it in a closed vessel

while slightly moistened, to a temperature of 200°C. or thereabouts. What takes place during this process, which is accompanied by a loss of weight amounting to about 10 per cent., I have never been able exactly to ascertain; but I have reason to believe that it consists in the total or partial destruction of one or more of the resinous colouring matters which act so prejudicially during the process of madder dyeing. Be this as it may, the effect is so great that if a certain quantity of madder be converted, first into garancine, and then by means of high pressure steam into the new product, the latter is found to act more efficiently, as far as the depth of permanent colour which it is capable of yielding, is concerned, than the original material from which it was prepared; or, in other words, a larger proportional quantity of madder must be used to produce the same ultimate effect.

As this subject is one, our knowledge of which is still far from complete, I have preferred on this occasion treating it historically rather than systematically, stating as concisely as I have been able, in what manner and by whom the various facts connected with it have been discovered. In doing so I must not pass over the labours of Dr. Debus, who in his interesting memoir on madder has given us the results of his investigation on its colouring matters, of which he distinguishes two, viz., *lizaric* and *oxylizaric acids*, which are identical with the alizarine and purpurine of other chemists.

There is another part of this subject which far exceeds in its intricacy as well as in the interest attaching to it that portion of which I have just given a short account; indeed much of it still remains involved in obscurity. The researches of modern chemists have made us acquainted with a number of highly complicated processes in which bodies derived from the organic world are concerned. Of these processes perhaps few are so difficult to comprehend, both as to their efficient causes and their results, as those in which fermentation plays a part. The process of alcoholic fermentation, one of the simplest cases, has been the object of study with many eminent chemists without any definite notion of its true nature being arrived at. Various other phenomena of fermentation besides the conversion of sugar into alcohol and carbonic acid have been discovered and investigated, such as the transformation of salicine into saligenine and sugar, of amygdaline into oil of bitter almonds, &c. That some process of this nature goes on in madder has long been suspected,

from the circumstance that when ground madder is kept for several years, it gradually improves in quality until it reaches a certain point, after which it again deteriorates. But what body it was that was acted on during this process, or what was the nature of the process remained quite unknown. Strecker supposes that the change which goes on consists in the conversion of alizarine into purpurine; but this would constitute anything but an improvement in quality, since the colours produced by purpurine are in most respects inferior to those of alizarine. Besides this, alizarine is a body not easily decomposed, unless exposed to the action of very potent agents, and any portion of it once formed in the root, would probably resist the action of air and moisture for a very long period of time, if not entirely. Mr. Higgin states, as the result of his experiments on this subject, that there exists in madder a peculiar albuminous ferment, which, by acting on the xanthine gives rise to the formation of colouring matter, and that this process takes place to some extent even during the short period of time occupied by dyeing. This statement I subsequently found to be a correct representation of the truth in its main features, and I think that to Mr. Higgin is due the first distinct enunciation of it.

That the whole of the colouring matter of madder does not exist ready-formed in the article as used by the dyer, may be rendered evident by a simple experiment. If madder be extracted with cold water, the clear watery extract does not contain any alizarine or other colouring matter, since these are almost insoluble in cold water. Nevertheless the extract when gradually heated is found capable of dyeing in the same way as madder itself. If the extract be made tolerably strong, it possesses a deep yellow colour and a very bitter taste; but if it be allowed to stand in a warm place for a few hours, it gelatinises, and the insoluble jelly which is formed is found to possess the whole of the tinctorial power of the liquid, while the latter has lost its yellow colour and bitter taste. Hence, it may be inferred that the substance which imparts to the extract its bitter taste and yellow colour is capable of giving rise to the formation of a certain portion of colouring matter. This simple fact formed the starting point of a fresh series of researches, of which I will in as few words as possible state the results. By extracting madder with boiling water, the subsequent gelatinisation or coagulation is prevented, and the extract retains its yellow colour and bitter taste, a proof that the

coagulation observed in the extract with cold water is a result of some process of fermentation which is arrested when the temperature is sufficiently raised. When the extract is agitated with a little animal charcoal, the latter absorbs the bitter principle and gives it up again to boiling spirits of wine, which on evaporation leaves it in an almost perfect state of purity. In this manner I obtained a substance, to which I have given the name of *Rubian*, and of which the principal characteristics are these:—It is amorphous and shining like gum, has a deep yellow colour and an intensely bitter taste, is easily soluble in water and alcohol. It is not a colouring matter in the practical sense of the word, for it gives to mordants in dyeing only the faintest shades of colour. But if its watery solution be mixed with sulphuric acid and boiled, it gradually deposits a quantity of insoluble yellow flocks and becomes almost colourless. These flocks after being well washed, are found to dye exactly the same colours as alizarine. In fact they contain alizarine. The liquid gives the reactions of sugar. Taking this fact into consideration, it becomes possible to give an account of all that takes place in the process of manufacturing garancine. It is evident that during this process, the easily soluble rubian becomes converted into the difficultly soluble alizarine, that there is in this case, in fact, an actual formation of colouring matter which is added to that which already exists in the root. A similar change takes place, when caustic alkali is used instead of the acid. A solution of rubian on being mixed with caustic potash or soda simply turns red, but on being boiled it becomes dark purple and deposits a purple powder which consists chiefly of a compound of alizarine with alkali, insoluble in caustic lye. Fermentation also decomposes rubian with great facility; but in order to effect its decomposition it is not indifferent what ferment be taken; a peculiar ferment is essential for the purpose. A solution of rubian may be left for several days in contact with yeast, decomposing albumen, casein, emulsin, &c., without showing any sign of change. But if an extract of madder with cold water be mixed with a large excess of alcohol, flocks of a dirty red colour are precipitated, which, after being well washed with alcohol are found to consist chiefly of an azotised principle which exerts a peculiar and powerful decomposing effect on rubian. If some of this substance be mixed with a watery solution of rubian, and the mixture be left to stand at the ordinary temperature, the rubian is found after a few hours

to be as completely decomposed as if it had been treated with a strong acid or caustic alkali, though no evolution of gas or any of the usual signs of fermentation have been manifested. The solution, if tolerably strong, gelatinises just as an extract of madder with cold water does under the same circumstances. The jelly when mixed with cold water is found to be almost insoluble. The water acquires only a slight colour, but contains sugar in solution, while the insoluble portion contains alizarine mixed with the ferment. With a knowledge of this process of decomposition it becomes possible to explain several curious phenomena, the true cause of which was previously unknown. It is well known to madder dyers that if the dye-bath be heated up rapidly to the boiling point, instead of gradually, as is the usual practice, prejudicial effects ensue. It is evident, from what I have just said, that the sudden heating puts a stop to the action of the ferment, as would be the case in any other process of fermentation, whereas the gradual heating allows it to exert its full decomposing power on the rubian. Hence, too, the advantage of mixing together several sorts of madder, one containing for instance an excess of rubian in proportion to ferment, the other a superabundance of ferment to counterbalance it, will be apparent. The improvement which takes place in the quality of madder after long keeping is probably also an effect of the same cause. Indeed, it seems highly probable that the alizarine, which undoubtedly exists ready formed in ordinary madder, owes its formation to the action of fermentation on rubian; and an experiment which I made with fresh madder roots goes far to prove that this is in fact the case, and that, surprising as it may seem, the fresh root contains no trace of ready-formed colouring matter. The experiment was as follows: Some madder roots having been taken out of the ground and cut small without being dried, produced the ordinary colours when used for dyeing in the common manner. But on treating the roots, after being cut into pieces as quickly as possible, with boiling alcohol, a yellow extract was obtained, which contained rubian, but which, even after all the alcohol had been driven away, was found incapable of imparting to mordants any but the slightest shades of colour; while the portion of the root left undissolved by the alcohol, on being subjected to the same test as the extract, imparted to mordants no more colour than the latter. It was evident, therefore, that the alcohol in this case had effected a separation between the colour-producing body and the agent

which under ordinary circumstances is destined to effect its transformation into colouring matter. The same relation, it is apparent, subsists between rubian and *erythrozym*, as I have called the ferment of madder, as between amygdaline and emulsine. It affords another of the instances of the mutual fitness of things and adaptation of means to an end, which we find occurring so often in all departments of nature, and which point so unmistakeably to an intelligence superior to our own. What, it may be asked, would have been the consequence if there had not been placed in close proximity with the colour-producing body of this plant another substance peculiarly fitted to effect its decomposition? Why, that probably one of the most valuable of our dyeing materials, and some of the most beautiful of our dyes would have remained for ages unknown, for it may be doubted whether, supposing this peculiar fermentative substance to have been absent in the root, we should ever, except by mere chance, have discovered the valuable properties of the latter.

The property which principally distinguishes erythrozym from other ferments is the power which it possesses of effecting the decomposition of rubian. When allowed to act on a watery solution of cane-sugar, the latter yields alcohol, carbonic acid, and hydrogen. The liquid is found to contain also a minute quantity of succinic acid, the formation of which I at one time supposed to be characteristic of this process of decomposition. Pasteur has however, since then discovered that this acid is always formed in small quantities during the ordinary fermentation of sugar by yeast. In its composition, erythrozym differs from all other known ferments. It contains carbon, hydrogen, nitrogen, and oxygen, but the proportion of nitrogen is remarkably small, as it hardly exceeds 4 per cent.

At first sight the change which rubian undergoes when decomposed by means either of acids, alkalies, or ferments, would seem to be simple enough. It might be supposed to consist simply in a splitting up of its complex molecule into alizarine and sugar, and to resemble many analogous processes with which we are acquainted, and which result in the formation of sugar and another body, the two together having formed originally a conjugate-compound. Nevertheless, the process is by no means so simple as might at first be supposed. The products of decomposition formed in these cases never consist of alizarine and sugar only. The part insoluble in cold water contains in all cases, besides

alizarine, two resinous bodies, one easily soluble in alcohol, which I call *Rubiretine*, the other less soluble in that liquid and to which, I have applied the name of *Verantine*. These bodies, though resembling resins in some respects, must be classed as colouring matters, since their colour seems to be inherent, and not a merely accidental property. But in addition to these, there is uniformly found accompanying the alizarine, a third body, belonging, as far as general appearance and properties are concerned, to the same class of substances as rubiacine. This third body is, however, in each case quite distinct. When acids have been employed for the decomposition of rubian, then this third body is found to have the following properties: It is tolerably soluble in boiling water, and crystallises in lemon-yellow, silky needles; it is decomposed on being heated, but resists the action of nitric and concentrated sulphuric acids; I have called it *Rubianine*. When alkalies are used instead of acids, then rubianine is replaced by *Rubiadine*, which is a body crystallising in beautiful, golden-yellow scales, insoluble in water, but soluble in alcohol, and is completely volatilised when heated. But when rubian is decomposed by fermentation, it yields neither of these two, but in their place *Rubiafine*, a substance resembling rubiadine in most of its properties, but essentially distinguished from it by passing into rubiacic acid when treated with perchloride of iron. This substance is usually accompanied by another of similar properties, of which it is difficult to say whether it must be considered as distinct from the others, since I have not succeeded in obtaining it in a state of perfect purity. I call it *Rubiagine*. Now all these bodies which accompany alizarine make their appearance so invariably on the occasions which I have named, that their occurrence cannot be considered as accidental. Let us see, therefore, how their simultaneous formation from rubian is to be explained. I assume for rubian the formula $C_{56}H_{34}O_{30}$. Hence it follows that rubian is converted into alizarine simply by the loss of 14 eqs. of water. The formation of verantine and rubiretine is due to another kind of decomposition. The formulæ of these two bodies being respectively $C_{28}H_{12}O_8$ and $C_{28}H_{10}O_{10}$, it will be seen that by adding both together we obtain 1 eq. of rubian, minus 12 of water. The composition of the class of bodies to which rubianine belongs is rather doubtful. It is probable that the formula of rubianine is $C_{44}H_{24}O_{20}$. If so, it is formed from rubian by the separation from the latter of 1 eq. of grape sugar. Rubiafine, however, being

easily convertible into rubiacic acid, must contain 32 eqs. of carbon, and its formula is therefore, probably, $C_{32}H_{13}O_9$, that of rubiadine being the same. In its conversion into these bodies, rubian therefore loses 2 eqs. of sugar, since $C_{56}H_{34}O_{30} + 3HO = C_{32}H_{13}O_9 + 3C_{12}H_{12}O_{12}$. It appears from this, that rubian undergoes, not one, but three different processes of decomposition when acted on by acids, alkalies, or ferments; that the formation of sugar is connected, not with that of alizarine, but with that of rubianine and its allies, and that in fact there is no reason why only one of these processes should not take place to the exclusion of the others,; why, for instance, rubian should not be so decomposed as to yield alizarine alone without any of the accompanying bodies, which are from this point of view, not only a source of loss, but also positively prejudicial in practice.

I am aware that the view which I take of the composition of rubian and its products is open to some objection. In the case of this, as of all other uncrystallisable organic bodies with very high atomic weights, doubts will arise in the mind of the chemist as to its right to be considered a pure unmixed substance. It might be supposed, for instance, that rubian, instead of being a pure substance, is a mixture, containing among other things a conjugate compound of alizarine and sugar, a view which has indeed been taken by Rochleder, and that the other products of decomposition are purely accidental. I may, therefore, very naturally be called on to adduce, if possible, further arguments in favour of the view I have taken, instead of basing it solely on such as are derived from an examination of the composition of these very complex bodies. I will, therefore, state in few words such as have occurred to me. In the first place, then, I have found that if the action of the ferment on rubian be retarded by means of antiseptic substances, the decomposition of the latter is not prevented, but there is then found no trace of alizarine among the products of decomposition, which then consist almost entirely of rubiretine and verantine. Now if rubian were a conjugated compound of alizarine and sugar, or contained any such compound, alizarine must of necessity appear among the products of the fermentation, however much this might be retarded.—2. If rubian contained the elements of sugar, it ought when decomposed with nitric acid to yield oxalic acid. Such is, however, not the case, when perfectly pure rubian is employed. The only product is phthalic acid, so that in this case rubian behaves as if

it contained alizarine only. The same takes place when hypochlorite of lime is the decomposing agent.—3. It is found that when chlorine is made to act on rubian, the phenomena are of a totally different description. By means of chlorine, rubian is converted into a yellow crystallised substance, almost insoluble in water, but soluble in alcohol, and almost neutral in its character, which I have called *Chlororubian*. Its formula is $C_{44}H_{27}ClO_{24}$, and it is consequently formed from rubian by the elimination of 1 atom of sugar and the replacement of 1 atom of hydrogen by 1 of chlorine. But chlororubian is itself also a glucoside; for by the action of strong acids, it splits up into grape sugar, which may be obtained from it with its usual crystalline appearance and other properties, and into a chlorinated body, possessing the properties of a weak acid, and which has the composition of rubiadine with 1 atom of hydrogen replaced by chlorine, hence called *chlororubiadine*. Rubian then, when decomposed by chlorine, behaves exactly as if it were a glucoside; it yields an atom of sugar and chlororubian, the latter of which, by decomposition with acids, gives another atom of sugar and a substitution product of one of the rubiadine series containing 32 atoms of carbon. No products of substitution standing in any relation to alizarine make their appearance, as far as my observations extend.* Now, if rubian behaves, when decomposed in one particular way, as if it contained alizarine only; when subjected to another kind of decomposition, as if rubiretine and verantine were its sole constituents; and when exposed to a third species of action, as if it were made up of sugar and one of the rubiadine class of bodies:

* Among the many anomalies with which this subject abounds, the following is deserving of mention. By the long-continued action of chlorine, chlororubian is converted into *perchlororubian*, a colourless crystallised substance, the formula of which is $C_{44}H_9Cl_9O_{15}$. Now it is singular that the 9 atoms of chlorine of this body are far more firmly combined with the other constituents than the 1 atom in chlororubian; for the latter, by the action of strong caustic alkalies loses the whole of its chlorine, which may also be detected by silver salts after treatment with nitric acid, whilst perchlororubian is not affected in the least degree either by caustic alkalies or by strong nitric acid. Chlororubian also is capable of combining with bases and plays the part of a weak acid, whilst perchlororubian, though containing 8 more atoms of chlorine, is a perfectly neutral substance, quite insoluble in caustic alkalies and not uniting with any base. Lastly, chlororubian is a glucoside, easily decomposed by strong acids and yielding sugar as one of its products of decomposition; whilst perchlororubian is not in the least affected by the strongest acids, the atoms which in chlororubian go to form sugar being, from some cause or other, prevented from doing so, after having entered into the composition of perchlororubian.

as to lead Professor Stokes, who has carefully examined them, to the conclusion that they cannot be produced by any compound of alizarine, or by a mixture of alizarine with any other substance hitherto obtained from madder. Nevertheless it is certain that alizarine and purpurine are nearly allied substances, since both of them yield phthalic acid when decomposed by nitric acid, a property which belongs, as far as is known, to no other substance with the exception of naphthaline. There is one property by which purpurine may be easily distinguished from alizarine, viz. that of being decomposed when its solution in caustic alkali is exposed to the air. The bright red colour of the solution, when left to stand in an open vessel, soon changes to reddish-yellow, and at length almost the whole of the colour disappears, after which the purpurine can no longer be discovered in the solution. This is probably the cause of the disappearance of purpurine, when the method given by me for the preparation of alizarine from madder and its separation from the impurities with which it is associated, is adopted. This method, which depends on the employment of caustic alkalies, is an imitation of that to which dyers have recourse for the purpose of improving and beautifying ordinary madder colours, and it is certain that during this process the purpurine is either decomposed or by some means disappears. The only advantage which purpurine presents over alizarine in dyeing is that it imparts to the alumina-mordant a fiery red tint which in some cases is preferred to the purplish-red colour from alizarine. To the iron mordant it communicates a very unsightly reddish-purple colour, presenting a disagreeable contrast with the lovely purple from alizarine. In all madder colours which have been subjected to a long course of after-treatment, the purpurine is found to have almost entirely disappeared.

For the purpose of convenient reference I have subjoined a table containing the formulæ, properties, and principal reactions of the various colouring matters, and their products of decomposition mentioned in the preceding pages.

Professor Stokes has had the kindness to draw up, for the purpose of being appended to this paper, the following account of the optical characters of purpurine and alizarine, containing the

	PHYSICAL PROPERTIES.	HEAT.	WATER.	ALCOHOL.	CHLORINE.	HYPOCHLORITE OF LIME.	CONCENTRATED SULPHURIC ACID.	DILUTE SULPHURIC OR MURIATIC ACID.	NITRIC ACID.	ALKALIES.	LIME AND BARYTA.	ALUMINA AND ITS SALTS.	PEROXIDE OF IRON AND ITS SALTS.	SALTS OF LEAD.	OTHER METALLIC SALTS.	FERMENTS.
Rubian $C_{56}H_{34}O_{30}$	Amorphoua, shining, brittle, not deliquescent, dark yellow, and transparent in thin layers, very bitter.	Begins to be decomposed at 130° C., gives a sublimate of alizarine and much charcoal.	Very easily soluble in water, removed from the solution by animal charcoal.	Not so easily soluble in alcohol as in water; separated by alcohol from its combination with animal charcoal.	Decomposed by chlorine, giving chlororubian and grape sugar.	Decomposed, giving phthalate of lime.	Dissolved with a blood-red colour, and decomposed on boiling the solution with blackening.	Decomposed on boiling, giving alizarine, rubiretine, verantine, rubianine and sugar.	Decomposed on boiling, giving phthalic acid.	Gives blood-red compounds with alkalies; decomposed by excess of caustic alkali, giving alizarine, rubiretine, verantine, rubiadine and sugar.	With lime and baryta water dark red precipitates, soluble in pure water.	Removed from its watery solution by excess of hydrate of alumina.	.. ..	With acetate of lead, watery solution gives no precipitate; with basic acetate of lead light red precipitate.	Alkaline solutions reduce salts of gold, but not salts of silver or copper.	Not affected by yeast, or decomposing casein, albumen, &c., but easily decomposed by erythrozym, giving alizarine, rubiretine, verantine, rubiafine, rubiagine and sugar.
Alizarine $C_{28}H_{10}O_8+6HO$	Crystallises in long transparent dark yellow needles, with much lustre.	At 100° C, loses its water of crystallisation and becomes opaque, at 216° C., begins to sublime, partly decomposed, leaving much charcoal.	Slightly soluble in boiling water with a yellow colour.	Soluble in boiling alcohol; solution is dark yellow, and when concentrated, deposits crystals on cooling and standing.	Decomposed by chlorine, and converted into a colourless substance.	.. ..	Dissolved in the cold with a yellow colour, and not decomposed on boiling the solution.	.. ..	Decomposed by boiling nitric acid, giving phthalic acid.	Dissolves in alkalies with violet colour; solutions in caustic alkalies do not change colour in the air; that in ammonia loses its ammonia.	Ammoniacal solution gives with chlorides of calcium and barium, purple precipitates.	Not more soluble in a boiling solution of alum than in boiling water; compound with alumina, not decomposed on boiling with weak caustic lye.	Peroxide of iron removes it from its solution in caustic potash or soda.	With acetate of lead, alcoholic solution gives a purple precipitate, which on standing becomes red.	Ammoniacal solution gives purple precipitates with salts of silver and copper; alcoholic solution becomes of beautiful purple with acetate of copper.	
Verantine $C_{28}H_{10}O_{10}$	Amorphous, pulverulent, reddish-brown.	Heated in a tube gives little oily sublimate and much charcoal.	Almost insoluble in cold and boiling water.	Soluble in boiling alcohol, and deposited again on cooling, as a brown powder.	.. ..	.. ..	Dissolved with a brown colour, and decomposed on boiling the solution, with blackening.	.. ..	Decomposed by concentrated nitric acid on boiling, not by dilute acid.	Soluble in alkalies with a dirty brownish-red colour.	Ammoniacal solution gives precipitates with lime and baryta salts.	.. ..	.. ..	With acetate of lead, alcoholic solution gives dark brown precipitate.		
Rubiretine $C_{28}H_{12}O_8$	Amorphous, resinous, brittle, opake, dark brown.	Softens at 100°C, then melts, then decomposed.	Very little soluble in cold and boiling water.	Easily soluble in cold alcohol.	.. ..	.. ..	Dissolved with a yellowish-brown colour, and decomposed on boiling the solution, with blackening.	.. ..	Decomposed by boiling nitric acid, and converted into a yellow substance, little soluble in alcohol.	Soluble in alkalies with a brownish-red colour.						
Rubianine $C_{44}H_{24}O_{20}$	Crystallises in bright lemon-yellow silky needles.	Heated in a tube gives little yellow crystalline sublimate and much charcoal.	Tolerably soluble in boiling water, crystallises out again on cooling.	Soluble in alcohol.	Decomposed by chlorine and converted into perchlororubian. (?)	.. ..	Dissolved with a yellow colour, and decomposed on boiling the solution, with blackening.	.. ..	Dissolved by boiling concentrated nitric acid, without being decomposed.	Dissolved with difficulty by alkalies, giving blood-red solutions.	Ammoniacal solution gives red precipitates with the chlorides of barium and calcium.	.. ..	Soluble in perchloride of iron solution, but not converted into rubiacic acid.	With acetate of lead, alcoholic solution gives no precipitate.		
Rubiadine $C_{32}H_{13}O_9$	Crystallises in yellow needles or in golden-yellow, glittering scales, or four-sided tables.	When heated, entirely volatilised, giving sublimate of yellow, micaceous shining scales.	Almost insoluble in boiling water.	More soluble in alcohol than rubianine.	.. ..	.. ..	Dissolved with a dark yellow colour, which changes to yellowish-brown on boiling.	.. ..	Decomposed by boiling nitric acid.	Behaves like rubianine.	The baryta compound crystallises in dark brownish-red needles soluble in water.	.. ..	Insoluble in perchloride of iron.	With acetate of lead, alcoholic solution gives no precipitate.		
Rubiacine $C_{32}H_{11}O_{10}$	Crystallises in greenish-yellow needles, or in tables with much lustre.	When heated, entirely volatilised, giving sublimate of brilliant yellow scales.	Slightly soluble in boiling water.	Soluble in boiling alcohol and crystallises out on cooling.	.. ..	.. ..	Dissolved with a yellow colour; not decomposed on boiling the solution.	.. ..	Dissolved by boiling dilute nitric acid without being decomposed.	Soluble in caustic alkalies, with a purple colour.	Ammoniacal solution gives with chlorides of calcium and barium red precipitates.	Removed from its alcoholic solution by excess of hydrate of alumina.	Dissolves in perchloride of iron with a dark brownish-red colour, and converted by boiling into rubiacic acid.	With acetate of lead, alcoholic solution gives a dark red precipitate.		
Rubiacic Acid $C_{32}H_9O_{17}$	Lemon-yellow powder, not crystalline.	When heated, gives no crystalline sublimate.	Slightly soluble in boiling water.	Slightly soluble in boiling alcohol.	.. ..	.. ..	Dissolved with a yellow colour, which becomes darker but not black on boiling the solution.	.. ..	Decomposed by boiling concentrated nitric acid.	The potash salt crystallises on cooling of its solution in boiling water, in long silky, brick-red needles; the colour of its watery solution is red, but changes to	Watery solution of the potash salt gives with chloride of calcium, a crystalline, orange-coloured precipitate, with chloride of barium a yellow precipitate	Watery solution of the potash salt gives with alum an orange-coloured precipitate.	Watery solution of the potash salt turns reddish-brown with perchloride of iron, but gives no precipitate.	.. ..	Watery solution of the potash salt gives with nitrate of silver a yellow precipitate, not changed on boiling the liquid; with sulphate of copper a red precipitate; with per-	

	bles.	ing scales.					boiling.										
Rubiacine $C_{32}H_{11}O_{10}$	Crystallises in greenish-yellow needles, or in tables with much lustre.	When heated, entirely volatilised, giving sublimate of brilliant yellow scales.	Slightly soluble in boiling water.	Soluble in boiling alcohol and crystallises out on cooling.	.. ..	.. ..	Dissolved with a yellow colour; not decomposed on boiling the solution.	.. ..	Dissolved by boiling dilute nitric acid without being decomposed.	Soluble in caustic alkalies, with a purple colour.	Ammoniacal solution gives with chlorides of calcium and barium red precipitates.	Removed from its alcoholic solution by excess of hydrate of alumina.	Dissolves in perchloride of iron with a dark brownish-red colour, and converted by boiling into rubiacic acid.	With acetate of lead, alcoholic solution gives a dark red precipitate.		
Rubiacic Acid $C_{32}H_9O_{17}$	Lemon-yellow powder, not crystalline.	When heated, gives no crystalline sublimate.	Slightly soluble in boiling water.	Slightly soluble in boiling alcohol.	.. ..	.. ..	Dissolved with a yellow colour, which becomes darker but not black on boiling the solution.	.. ..	Decomposed by boiling concentrated nitric acid.	The potash salt crystallises on cooling of its solution in boiling water, in long silky, brick-red needles; the colour of its watery solution is red, but changes to purple on the addition of caustic potash; the salt is decomposed on heating, with a slight explosion.	Watery solution of the potash salt gives with chloride of calcium, a crystalline, orange-coloured precipitate, with chloride of barium a yellow precipitate.	Watery solution of the potash salt gives with alum an orange-coloured precipitate.	Watery solution of the potash salt turns reddish-brown with perchloride of iron, but gives no precipitate.	.. ..	Watery solution of the potash salt gives with nitrate of silver a yellow precipitate, not changed on boiling the liquid; with sulphate of copper a red precipitate; with perchloride of mercury a yellow crystalline precipitate.	
Rubiafine $C_{32}H_{13}O_9$	Crystallises in yellow shining needles and scales.	When heated, entirely volatilised, giving yellow crystalline sublimate.	Very little soluble in boiling water.	Soluble in boiling alcohol and crystallises out on cooling.	.. ..	.. ..	Dissolved, not decomposed on boiling the solution.	.. ..	Dissolved by boiling nitricacid, not decomposed.	Soluble in caustic alkalies with a reddish-purple, in carbonated alkalies with a red colour.	.. ..	.. ..	Dissolves in perchloride of iron with dark brownish-purple colour, and converted by boiling into rubiacic acid.	With acetate of lead, alcoholic solution gives a crimson precipitate.	With acetate of copper, alcoholic solution gives an orange-coloured precipitate.	
Rubiagine	Crystallises in yellow needles collected in grains and nodules.	When heated, gives little crystalline sublimate and much charcoal.	Insoluble in boiling water.	Easily soluble in boiling alcohol, not crystallising on cooling.	.. ..	.. ..	Dissolved with a reddish-brown colour, decomposed on boiling the solution, with blackening.	.. ..	Dissolved by boiling nitricacid, solution on cooling depositing yellow shining needles.	Soluble in alkalies with a blood-red colour.	Soluble in lime and baryta water with blood-red colour.	.. ..	Very little soluble in perchloride of iron.	With acetate of lead, alcoholic solution turns dark yellow, and after some time gives orange-coloured granular precipitates.	With acetate of copper, behaves like rubiafine.	
Rubianic Acid $C_{52}H_{29}O_{27}$	Crystallises in lemon-yellow silky needles.	When heated, gives sublimate of alizarine and much charcoal.	Soluble in boiling water and crystallises out again on cooling; watery solution is bitter and reddens litmus paper.	Soluble in alcohol.	Decomposed slowly by chlorine, products of decomposition being soluble in water.	.. ..	Dissolved with a dark red colour, which becomes reddish-brown on boiling the solution, little sulphurous acid being evolved.	Decomposed on boiling, giving alizarine and sugar.	Decomposed by boiling nitricacid, with facility.	Dissolves in caustic alkalies with cherry-red colour, which on boiling changes to purple, alizarine and sugar being formed; with carbonate of potash, gives silky puce-coloured needles of potash salt.	Watery solution gives with lime water a light red precipitate; with baryta water a crimson precipitate.	Watery solution gives no precipitate with acetate of alumina.	Dissolves in perchloride of iron with a greenish-brown colour, the solution containing protochloride.	With acetate of lead, watery solution turns red without giving any precipitate; with basic acetate it gives a copious red precipitate.	Alkaline solutions reduce salts of gold, but not salts of silver.	Decomposed by erythrozym, giving alizarine and sugar.
Chlororubian $C_{44}H_{27}ClO_{24}$	Crystallises in orange-coloured needles, slightly bitter on being chewed.	When heated, gives a little white crystalline sublimate and much charcoal.	Soluble in boiling water and deposited on cooling in amorphous masses.	Soluble in boiling alcohol, crystallises out on cooling; solution does not redden litmus paper.	Converted by chlorine into perchlororubian.	.. ..	.. ..	Decomposed on boiling, giving chlororubiadine and grape sugar.	Decomposed by boiling nitric acid, giving colourless solution, from which nitrate of silver precipitates chloride of silver.	Soluble in alkalies with a blood-red colour; converted by excess of caustic alkali into oxyrubian, with loss of its chlorine.	Watery solution turns red with lime water; with baryta water it turns red, and on boiling deposits red flakes and becomes colourless.	Watery solution gives no precipitate with acetate of alumina.	Soluble in perchloride of iron with a brownish-yellow colour, becoming after some time dark brown.	With acetate of lead, alcoholic solution gives no precipitate; with basic acetate, watery solution gives red precipitate.	Watery solution gives no precipitate with nitrate of silver.	
Chlororubiadine $C_{32}H_{12}ClO_9$	Crystallises in small yellow needles and scales.	When heated, gives acid fumes and a little crystalline sublimate, and leaves much charcoal.	Insoluble in boiling water.	Soluble in boiling alcohol and crystallises out again on cooling; solution reddens blue litmus paper.	Converted by chlorine into a dark yellow, amorphous, resinous substance, insoluble in water, but easily soluble in alcohol.	.. ..	Dissolved with an orange colour, which becomes dark purple on boiling the solution.	.. ..	Dissolved by nitric acid, of sp. gr. 1·52 in the cold; the solution gives no precipitate with nitrate of silver, but on boiling chloride of silver precipitates.	Soluble in caustic fixed alkalies with a purplish-red colour, and in ammonia and carbonated alkalies with a blood-red colour.	The baryta compound, formed by double decomposition, crystallises from water in long red needles, arranged in fan-shaped masses.	Alcoholic solution gives no precipitate with acetate of alumina.	Insoluble in perchloride of iron.	With acetate of lead alcoholic solution gives no precipitate, even on adding ammonia also.	Alcoholic solution gives with acetate of copper a copious light brown precipitate.	
	Crystallises in colourless, transparent, flat, four-	When slowly heated, entirely volatilised, giving	Insoluble in boiling water.	Soluble in boiling alcohol and crystallises out	.. ..	.. ..	Dissolved, not decomposed on boiling the solu-	.. ..	Dissolved by nitric acid, of sp. gr. 1·52; not de-	Insoluble in alkalies.	.. ..	.. ..	.. ..	With acetate of lead, alcoholic so-		

	Crystallises in …	… entirely volatilised …	… in boiling …	… crystallises out …			boiling the solution.		gr. 1·52; not decomposed on boiling the solution.	dition of caustic potash; the salt is decomposed on heating, with a slight explosion.					… crystalline precipitate.	
Rubiafine $C_{32}H_{13}O_9$	Crystallises in yellow shining needles and scales.	When heated, entirely volatilised, giving yellow crystalline sublimate.	Very little soluble in boiling water.	Soluble in boiling alcohol and crystallises out on cooling.	.. ..	.. ..	Dissolved, not decomposed on boiling the solution.	.. ..	Dissolved by boiling nitric acid, not decomposed.	Soluble in caustic alkalies with a reddish-purple, in carbonated alkalies with a red colour.	.. ..	.. ..	Dissolves in perchloride of iron with dark brownish-purple colour, and converted by boiling into rubiacic acid.	With acetate of lead, alcoholic solution gives a crimson precipitate.	With acetate of copper, alcoholic solution gives an orange-coloured precipitate.	
Rubiagine	Crystallises in yellow needles collected in grains and nodules.	When heated, gives little crystalline sublimate and much charcoal.	Insoluble in boiling water.	Easily soluble in boiling alcohol, not crystallising on cooling.	.. ..	.. ..	Dissolved with a reddish-brown colour, decomposed on boiling the solution, with blackening.	.. ..	Dissolved by boiling nitric acid, solution on cooling depositing yellow shining needles.	Soluble in alkalies with a blood-red colour.	Soluble in lime and baryta water with blood-red colour.	.. ..	Very little soluble in perchloride of iron.	With acetate of lead, alcoholic solution turns dark yellow, and after some time gives orange-coloured granular precipitates.	With acetate of copper, behaves like rubiafine.	
Rubianic Acid $C_{52}H_{29}O_{27}$	Crystallises in lemon-yellow silky needles.	When heated, gives sublimate of alizarine and much charcoal.	Soluble in boiling water and crystallises out again on cooling; watery solution is bitter and reddens litmus paper.	Soluble in alcohol.	Decomposed slowly by chlorine, products of decomposition being soluble in water.	.. ..	Dissolved with a dark red colour, which becomes reddish-brown on boiling the solution, little sulphurous acid being evolved.	Decomposed on boiling, giving alizarine and sugar.	Decomposed by boiling nitric acid, with facility.	Dissolves in caustic alkalies with cherry-red colour, which on boiling changes to purple, alizarine and sugar being formed; with carbonate of potash, gives silky puce-coloured needles of potash salt.	Watery solution gives with lime water a light red precipitate; with baryta water a crimson precipitate.	Watery solution gives no precipitate with acetate of alumina.	Dissolves in perchloride of iron with a greenish-brown colour, the solution containing protochloride.	With acetate of lead, watery solution turns red without giving any precipitate; with basic acetate it gives a copious red precipitate.	Alkaline solutions reduce salts of gold, but not salts of silver.	Decomposed by erythrozym, giving alizarine and sugar.
Chlororubian $C_{44}H_{27}ClO_{24}$	Crystallises in orange-coloured needles, slightly bitter on being chewed.	When heated, gives a little white crystalline sublimate and much charcoal.	Soluble in boiling water and deposited on cooling in amorphous masses.	Soluble in boiling alcohol, crystallises out on cooling; solution does not redden litmus paper.	Converted by chlorine into perchlororubian.	.. ..	.. ..	Decomposed on boiling, giving chlororubiadine and grape sugar.	Decomposed by boiling nitric acid, giving colourless solution, from which nitrate of silver precipitates chloride of silver.	Soluble in alkalies with a blood-red colour; converted by excess of caustic alkali into oxyrubian, with loss of its chlorine.	Watery solution turns red with lime water; with baryta water it turns red, and on boiling deposits red flakes and becomes colourless.	Watery solution gives no precipitate with acetate of alumina.	Soluble in perchloride of iron with a brownish-yellow colour, becoming after some time dark brown.	With acetate of lead, alcoholic solution gives no precipitate; with basic acetate, watery solution gives red precipitate.	Watery solution gives no precipitate with nitrate of silver.	
Chlororubiadine $C_{32}H_{12}ClO_9$	Crystallises in small yellow needles and scales.	When heated, gives acid fumes and a little crystalline sublimate, and leaves much charcoal.	Insoluble in boiling water.	Soluble in boiling alcohol and crystallises out again on cooling; solution reddens blue litmus paper.	Converted by chlorine into a dark yellow, amorphous, resinous substance, insoluble in water, but easily soluble in alcohol.	.. ..	Dissolved with an orange colour, which becomes dark purple on boiling the solution.	.. ..	Dissolved by nitric acid, of sp. gr. 1·52 in the cold; the solution gives no precipitate with nitrate of silver, but on boiling chloride of silver precipitates.	Soluble in caustic fixed alkalies with a purplish-red colour, and in ammonia and carbonated alkalies with a blood-red colour.	The baryta compound, formed by double decomposition, crystallises from water in long red needles, arranged in fan-shaped masses.	Alcoholic solution gives no precipitate with acetate of alumina.	Insoluble in perchloride of iron.	With acetate of lead alcoholic solution gives no precipitate, even on adding ammonia also.	Alcoholic solution gives with acetate of copper a copious light brown precipitate.	
Perchlororubian $C_{44}H_9Cl_9O_{15}$	Crystallises in colourless, transparent, flat, four-sided iridescent tables.	When slowly heated, entirely volatilised, giving a sublimate of bright micaceous scales; suddenly heated it is decomposed with slight explosion.	Insoluble in boiling water.	Soluble in boiling alcohol and crystallises out again on cooling.	.. ..	.. ..	Dissolved, not decomposed on boiling the solution.	.. ..	Dissolved by nitric acid, of sp. gr. 1·52; not decomposed on boiling the solution.	Insoluble in alkalies.	.. ..	.. ..	.. ..	With acetate of lead, alcoholic solution gives no precipitate.		
Purpurine	Crystallises in small orange-coloured or red needles.	When heated carefully, it is volatilised without much residue, giving a sublimate of shining scales and needles.	Slightly soluble in boiling water with a pink colour.	Soluble in boiling water and crystallises out on cooling.	.. ..	.. ..	Dissolved, not decomposed on boiling the solution.	.. ..	Decomposed by boiling dilute nitric acid, more easily than alizarine.	Soluble in alkalies with bright purplish-red colour; solutions in caustic fixed alkalies lose their colour by the action of oxygen.	Ammoniacal solution gives with chlorides of calcium and barium, purple precipitates.	Soluble in boiling alum-liquor with a pink colour, not separating on cooling, but precipitated by muriatic acid.	.. ..	With acetate of lead, alcoholic solution gives a purple precipitate, not changed on standing, which dissolves on boiling with excess of acetate of lead, giving a purple solution.		

results obtained by him on a renewed examination of their action on light.

Optical Characters of Purpurine and Alizarine.

The optical characters of purpurine are distinctive in the very highest degree; those of alizarine are also very distinctive. The characters here referred to consist in the mode of absorption of light by certain solutions of the bodies, and occasionally in the powerful fluorescence of a solution. They are specially valuable because their observation is independent of more than a moderate degree of purity of the specimens, and requires no apparatus beyond a test-tube, a slit, and a small prism, a little instrument which ought to be in the hands of every chemist.

Alkaline solution of purpurine.—If purpurine be dissolved in a solution of carbonate of potash or soda, (it is easily decomposed by caustic alkalies,) the solution obtained absorbs with greatest energy the green part of the spectrum. In this and similar cases it is necessary to take care either to use a sufficiently small quantity of the substance, or else to dilute sufficiently the solution, or view it through a sufficiently small thickness; otherwise a broad region of the spectrum is absorbed, and the peculiar characters of the substance depending on its mode of absorbing light are not perceived. If the solution be contained in a wedge-shaped vessel, the effect of different thicknesses is seen at a glance; but a test-tube will answer perfectly well if two or three different degrees of dilution be tried in succession. When the light transmitted through an alkaline solution of purpurine of suitable

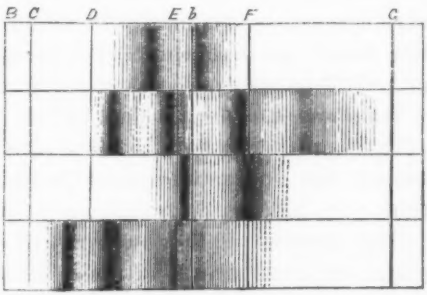

FIG. 1.—Solution of purpurine in carbonate of soda or potash, or in alum-liquor.

FIG. 2.—Solution of purpurine in bisulphide of carbon.

FIG. 3.—Solution of purpurine in ether.

FIG. 4.—Alkaline solution of alizarine.

strength, after being limited by a slit, is viewed through a prism, two remarkable dark bands of absorption (Fig. 1) are seen about

the green part of the spectrum, comprising between them a band of green light, which, though much weakened in comparison with the same part of the unabsorbed spectrum, is bright compared with the two dark bands, which latter in a sufficiently strong solution appear perfectly black. The places of the dark bands, estimated with reference to the principal fixed lines of the spectrum, are given in the figure.

Solution in a solution of alum.—This solution has the same peculiar mode of absorption, and (Fig. 1) will serve equally well for it. But it has the further property of being eminently fluorescent, which the alkaline solution is not at all. The fluorescent light is yellow, but ordinarily appears orange from being seen through the fluid. The difference between the alkaline and alum-liquor solutions as to fluorescence does not depend on the acid reaction of the latter, but on the alumina. A solution exhibiting to perfection the peculiar properties of the alum-liquor solution may be obtained by adding to a solution of purpurine in carbonate of soda a solution of alum to which enough tartaric acid to prevent precipitation, and then carbonate of soda, has previously been added; and in this case the fluorescent solution is obtained at once and in the cold. This forms a very striking reaction in a dark room, according to the method described in the *Philosophical Transactions for* 1853, p. 385, with the combination, solution of nitrate of copper and a red (Cu_2O) glass. Some other colourless oxides besides alumina develop in this manner fluorescence, though to a less degree.

Solution in bisulphide of carbon.—This solution gives the highly characteristic spectrum (Fig. 2) exhibiting four bands of absorption, of which the first is narrower than the others, and the fourth is very inconspicuous, hardly standing out from the general absorption which takes place in that region of the spectrum. The second and third bands are the most conspicuous of the set.

Solution in ether.—This gives the characteristic spectrum (Fig. 3) exhibiting two bands of absorption. The solution is fluorescent, but not enough so to be perceptible by common observation.

The spectra of the solutions of purpurine in other solvents might be mentioned, but these are more than sufficient. In an optical point of view purpurine is remarkable for the general similarity of character, combined with diversity as to detail, which its various solutions exhibit as to their mode of absorbing light.

Alkaline solution of alizarine.—The solution of alizarine in caustic or carbonate of potash or soda, or in ammonia, exhibits on analysis the characteristic spectrum (Fig. 4) having a band of absorption in the yellow, and another narrower one between the red and the orange. There is a third very inconspicuous band at E, almost lost in the general darkening of that part of the spectrum.

Other solutions.—The solution of alizarine in ether or in bisulphide of carbon shows nothing particular. There is a general absorption of the more refrangible part of the spectrum, but there are none of those remarkable alternations of comparative transparency and opacity which characterize purpurine. Alizarine is hardly soluble in alum-liquor; and in the case of the red solution of mixed alizarine and verantine mentioned by Dr. Schunck at page 451 of the *Philosophical Transactions for* 1851, the absence of the remarkable absorption-bands (Fig. 1) and the absence of fluorescence, show instantly and independently of each other that it is distinct from purpurine.

Optical detection of purpurine and alizarine.—The characters of these substances are so marked that I do not know any substance with which either of them could be confounded, even if we restricted ourselves to *any one* of the solutions yielding the peculiar spectra. Not only so, but these properties enable us to detect small quantities, in the case of purpurine the merest trace, of the substance, present in the midst of a quantity of impurities. In the case of purpurine, a solution of alum is specially convenient for use, because the impurities liable to be present do not with this solvent absorb the part of the spectrum in which the bands occur. In this way I was able, though operating on only a very minute quantity of the root, to detect purpurine in more than twenty species of the family *Rubiaceæ* which were examined with this view, comprising the genera *Rubia, Asperula, Galium, Crucianella,* and *Sherardia.* The detection of alizarine by means of the characters of its alkaline solution is much less delicate, because many of the impurities liable to be present absorb the part of the spectrum in which all but the least refrangible of the absorption-bands occur; and as this band is not that which corresponds to the most intense absorption, a larger quantity of the substance must be present in order that the band may be perceived.

XXI.—*On the Polyatomic Alcohols.*

A Discourse delivered before the Fellows of the Chemical Society of London.

By Dr. H. Debus, F.C.S.

The polyatomic alcohols are derived by replacing in n atoms of water n atoms of hydrogen, by an n-atomic basic radical, consisting either of carbon and hydrogen, or of carbon, hydrogen, and oxygen.* For glycol, which contains the diatomic radical C_2H_4, we have $n = 2$.

$$\underset{\text{2 At. of water.}}{\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2} \qquad \underset{\text{Glycol.}}{\left.\begin{matrix}(C_2H_4)''\\H_2\end{matrix}\right\}O_2}$$

And if we assume glycerine to contain the triatomic radical C_3H_5, the formula for glycerine will be—

$$\underset{\text{3 At. of water.}}{\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3} \qquad \underset{\text{Glycerine.}}{\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3}$$

Compounds among the acids, the polybasic acids, which correspond to the polyatomic alcohols, have been known for several years. Mr. Graham's excellent researches on phosphoric acid and the phosphates led him to the conception of his theory of polybasic acids, which was afterwards adopted and further developed by Liebig. Our present mode of viewing these bodies, is chiefly founded on the investigations of Gerhardt and Williamson. The doctrine of polyatomic alcohols principally owes its development to the researches of Wurtz and Berthelot, undertaken within the last few years.

A. *Diatomic Alcohols.*

Glycol,† the first body of this class, was obtained three years ago by Wurtz, by placing iodide of ethylene‡ in contact with

* n is considered to represent a number greater than 1.

† Compt. rend. xliii, 199; Inst. 1856, 277; Ann. Ch. Pharm., c, 110.

‡ Faraday (1821), Ann. Phil. xviii, 118; Regnault, Ann. Chim. Phys. lix, 367.

acetate of silver; a lively reaction takes place, iodide of silver and acetate of glycol being produced:

$$\underbrace{\left.\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O \\ \left.\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O}_{\text{2 At of acetate of silver.}} + \underbrace{(C_2H_4)''I_2}_{\text{Iodide of ethylene.}} = \underbrace{\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\\C_2H_3O\end{matrix}\right\}O_2}_{\text{Diacetate of glycol.}} + \underbrace{2\,AgI}_{\text{Iodide of silver.}}$$

The diatomic radical ethylene replaces the two atoms of silver in two atoms of acetate of silver, and thus unites the two molecules to form acetate of glycol. Iodide of ethylene stands to diacetate of glycol in the same relation as iodide of ethyle to acetic ether.*

$$\underbrace{(C_2H_4)''I_2}_{\text{Iodide of ethylene.}} \qquad \underbrace{C_2H_5I}_{\text{Iodide of ethyle.}}$$

$$\underbrace{\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\\C_2H_3O\end{matrix}\right\}O_2}_{\text{Diacetate of glycol.}} \qquad \underbrace{\left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right\}O}_{\text{Acetate of ethyle.}}$$

If diacetate of glycol be distilled with hydrate of potash at 250° C., acetate of potash and glycol are obtained.

$$\underbrace{\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\\C_2H_3O\end{matrix}\right\}O_2}_{\text{Diacetate of glycol.}} + \underbrace{\left.\begin{matrix}K\\H\end{matrix}\right\}O \\ \left.\begin{matrix}K\\H\end{matrix}\right\}O}_{\text{Hydrate of potash.}} = \underbrace{\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2}_{\text{Glycol.}} + \underbrace{\left.\begin{matrix}K\\C_2H_3O\end{matrix}\right\}O \\ \left.\begin{matrix}K\\C_2H_3O\end{matrix}\right\}O}_{\text{Acetate of potash.}}$$

The best mode obtaining monacetate of glycol, is by Dr. Atkinson's process,† which consists in heating an alcoholic solution of one atom of bromide of ethylene with two atoms of acetate of potash, enclosed in a soda-water bottle, for two days at 100° C. The liquid is separated from the bromide of potassium, subjected to distillation, and those portions are collected as monacetate of glycol which come over at 182° C.

* $(C_2H_4)''Cl_2$ and $(C_2H_4)''Br_2$, contain in equal volumes of their vapours twice as much chlorine and bromine as C_2H_5Cl and C_2H_5Br.

† Phil. Mag. Dec. 1858; Ann. Ch. Pharm. cix, 232.

$$\underbrace{\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O \\ \left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O}_{\text{Acetate of potash.}} + \underbrace{(C_2H_4)''Br_2}_{\text{Bromide of ethylene.}} = \underbrace{\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\\C_2H_3O\end{matrix}\right\}O_2}_{\text{Diacetate of glycol.}} + 2KBr$$

$$\underbrace{\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\\C_2H_3O\end{matrix}\right\}O_2}_{\text{Diacetate of glycol.}} + \underbrace{\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O}_{\text{Alcohol.}} = \underbrace{\left.\begin{matrix}H\\(C_2H_4)''\\C_2H_3O\end{matrix}\right\}O_2}_{\text{Monacetate of glycol.}} + \underbrace{\left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right\}O}_{\text{Acetate of ethyle.}}$$

By distilling monacetate of glycol with hydrate of potash, glycol can easily be prepared.* In a similar manner, the following glycols homologous to ethylo-glycol, have been obtained.

$\left.\begin{matrix}(C_3H_6)''\\H_2\end{matrix}\right\}O_2$, from propylene.† $\left.\begin{matrix}(C_4H_8)''\\H_2\end{matrix}\right\}O_2$, from butylene.‡

$\left.\begin{matrix}(C_5H_{10})''\\H_2\end{matrix}\right\}O_2$, from amylene.§

These bodies are syrupy liquids, volatile without decomposition, and soluble in water and ethylic alcohol. Ethylo-glycol boils at 197° C., propylo-glycol at 188° C., and amylo-glycol at 177° C.. The exceptional property of this class of homologous substances, to boil at a lower temperature, as they become richer in carbon and hydrogen, is very remarkable. Compounds of these glycols have been obtained by the action of the chlorides, bromides, or iodides of ethylene, propylene or amylene, on certain potash or silver salts; also by the action of acids on these glycols; and by decomposing potassium or sodium-glycol with iodides.

Chemical Properties of the Glycols.

1. With monatomic acids, they form two ethers by the successive replacement of two atoms of hydrogen by monatomic acid radicals.

* Ann. Ch. Pharm. cx, 317–8.

† Compt. rend. xlv, 306; Inst. 1857, 300; Ann. Ch. Pharm. cv, 202.

‡ Compt. rend. xlvi, 244.

§ Ann. Ch. Pharm. cvi, 24.

$$\left.\begin{matrix} H \\ (C_2H_4)'' \\ H \end{matrix}\right\} O_2 \qquad \left.\begin{matrix} H \\ (C_2H_4)'' \\ C_2H_3O \end{matrix}\right\} O_2 \qquad \left.\begin{matrix} C_2H_3O \\ (C_2H_4)'' \\ C_2H_3O \end{matrix}\right\} O_2$$

Glycol. Monacetate of glycol. Diacetate of glycol.

a. Compound obtained by replacing in glycol *one* atom of hydrogen by a monatomic acid radical.*

$$\left.\begin{matrix} H \\ (C_2H_4)'' \\ C_2H_3O \end{matrix}\right\} O_2, \quad \text{Monacetate of glycol.}$$

Monacetate of glycol is formed, not only by the action of bromide of ethylene on acetate of potash, but also by heating equivalent quantities of glycol and anhydrous acetic acid at temperatures not exceeding 170° C.

b. Compounds obtained by replacing in glycols *two* atoms of hydrogen by two monatomic acid radicals, either of the same or of a different kind.†

$\left.\begin{matrix} C_2H_3O \\ (C_2H_4)'' \\ C_2H_3O \end{matrix}\right\} O_2$ Diacetate of ethylo-glycol. $\left.\begin{matrix} C_2H_3O \\ (C_3H_6)'' \\ C_2H_3O \end{matrix}\right\} O_2$ Diacetate of propylo-glycol.

$\left.\begin{matrix} C_2H_3O \\ (C_4H_8)'' \\ C_2H_3O \end{matrix}\right\} O_2$ Diacetate of butylo-glycol. $\left.\begin{matrix} C_2H_3O \\ C_5H_{10} \\ C_2H_3O \end{matrix}\right\} O_2$ Diacetate of amylo-glycol.

These four compounds are formed by the action of the bromides of the radicals C_2H_4, C_3H_6, C_4H_8, and C_5H_{10}, on acetate of silver.

Here also may be mentioned sulphocyanide of ethylene.‡

$$\left.\begin{matrix} Cy \\ (C_2H_4)'' \\ Cy \end{matrix}\right\} S_2$$

Brüning obtained, by the action of an alcoholic solution of potash on iodoform, a substance to which he attributes the formula

$$\left.\begin{matrix} CHI_2 \\ CHI_2 \end{matrix}\right\} O$$

* Atkinson. Phil. Mag., Dec., 1858.

† Wurtz. Compt. rend. xlvi, 244; xlv, 306; xliii, 199; Ann. Ch. Pharm. c, 112; cv, 203; cvi, 25.

‡ Buff. Ann. Ch. Pharm. xcvi, 302; c, 229; Chem. Gaz. (1856), 416; Phil. Mag. [4] xiii, 374.

The same body was prepared by Buttlerow from iodoform and ethylate of sodium, but he represents it as diiodide of methylene, CH_2I_2. With acetate of silver, it furnished iodide of silver and a liquid which distilled at about 170° C., and which Buttlerow considers to be diacetate of methylo-glycol. The latter, treated with baryta yielded, not methylo-glycol, but acetate and formiate of baryta. This subject requires further examination.*

2. If glycol and hydrochloric acid be heated together, water and chlorhydrine of glycol are formed.†

$$\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2 + HCl = \underbrace{\left.\begin{matrix}H\\(C_2H_4)''\end{matrix}\right\}O,Cl}_{\text{Chlorhydrine of glycol.}} + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Chlorhydrine of glycol will probably yield, by renewed treatment with hydrochloric acid, under suitable conditions, dichloride of ethylene and water.

$$\left.\begin{matrix}H\\(C_2H_4)''\end{matrix}\right\}O,Cl + HCl = (C_2H_4)''Cl_2 + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Propylo-glycol and hydrochloric acid form chlorhydrine of propylo-glycol and water.

$$\left.\begin{matrix}H\\(C_3H_6)''\\H\end{matrix}\right\}O_2 + HCl = \left.\begin{matrix}H\\(C_3H_6)''\end{matrix}\right\}O,Cl + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Sulphuric acid, which is bibasic, and like glycol is derived from two atoms of water, yields similar derivatives.

$$\underbrace{\left.\begin{matrix}H\\(SO_2)''\\H\end{matrix}\right\}O_2}_{\text{Sulphuric acid.}} \qquad \underbrace{\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2}_{\text{Glycol.}}$$

$$\underbrace{\left.\begin{matrix}H\\(SO_2)''\end{matrix}\right\}O,Cl‡}_{\text{Intermediate compound.}} \qquad \underbrace{\left.\begin{matrix}H\\(C_2H_4)''\end{matrix}\right\}O,Cl}_{\text{Intermediate compound.}}$$

$$\underbrace{(SO_2)'',Cl_2}_{\text{Dichloride of sulphuryle.}} \qquad \underbrace{(C_2H_4)'',Cl_2}_{\text{Dichloride of ethylene.}}$$

* Ann. Ch. Pharm. cxi, 242. (August, 1859.)

† Compt. rend. xlviii, 101; Ann. Ch. Pharm. cx, 125.

‡ Williamson. Chem. Soc. Qu. J. vii, 180; Proc. R. S. vii, 11; Ann. Ch. Pharm. xcii, 242.

Hydriodic acid and glycol form, according to temperatures, either iodide of ethylene or iodhydrine of glycol, and water.

$$\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2 + 2\,HI = (C_2H_4)''I_2 + 2\left.\begin{matrix}H\\H\end{matrix}\right\}O$$

$$\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2 + HI = \underbrace{\left.\begin{matrix}H\\(C_2H_4)''\end{matrix}\right\}O,I}_{\text{Iodhydrine of glycol.}} + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Chlorhydrine of glycol is rapidly decomposed by caustic potash, chloride of potassium, oxide of ethylene and water being produced.

$$\left.\begin{matrix}H\\(C_2H_4)''\end{matrix}\right\}O,Cl + KHO = KCl + \left.\begin{matrix}H\\H\end{matrix}\right\}O + \underbrace{(C_2H_4)''O}_{\text{Oxide of ethylene.}}$$

Oxide of ethylene is isomeric with, and has the same vapour density as acetic aldehyde. Oxide of ethylene is decomposed with great violence by pentachloride of phosphorus, dichloride of ethylene and oxychloride of phosphorus being produced.

$$(C_2H_4)''O + PCl_5 = (C_2H_4)''Cl_2 + PCl_3O$$

From oxide of ethylene, glycol compounds can be regenerated, which substances Wurtz could not obtain from aldehyde. Pentachloride of phosphorus and acetic aldehyde furnish a body which has the composition of dichloride of ethylene, but it is only isomeric, and not identical with Dutch liquid. Probably oxide of ethylene is the ether of glycol, for it stands to this alcohol as anhydrous sulphuric acid does to—

$$\left.\begin{matrix}H\\(SO_2)''\\H\end{matrix}\right\}O_2$$

A substance, which would bear the same relation to glycol as common ether bears to ethylic alcohol, might be obtained by the action of dichloride of ethylene on—

$$\left.\begin{matrix}Na\\(C_2H_4)''\\Na\end{matrix}\right\}O_2$$

$$\left.\begin{matrix}\mathrm{Na}\\(\mathrm{C_2H_4})''\\\mathrm{Na}\end{matrix}\right\}\mathrm{O_2} + (\mathrm{C_2H_4})''\mathrm{Cl_2} = \left.\begin{matrix}(\mathrm{C_2H_4})''\\(\mathrm{C_2H_4})''\end{matrix}\right\}\mathrm{O_2} + 2\,\mathrm{NaCl}$$

$$\left.\begin{matrix}(\mathrm{C_2H_4})''\\(\mathrm{C_2H_4})''\end{matrix}\right\}\mathrm{O_2} \qquad \left.\begin{matrix}\mathrm{C_2H_5}\\\mathrm{C_2H_5}\end{matrix}\right\}\mathrm{O}$$

$$\left.\begin{matrix}\mathrm{H}\\(\mathrm{C_2H_4})''\\\mathrm{H}\end{matrix}\right\}\mathrm{O_2} \qquad \left.\begin{matrix}\mathrm{C_2H_5}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$$

The decomposition of chlorhydrine of propylo-glycol with caustic potash, yields oxide of propylene;

$$\left.\begin{matrix}\mathrm{H}\\(\mathrm{C_3H_6})''\end{matrix}\right\}\mathrm{O,Cl} - \mathrm{HCl} = (\mathrm{C_3H_6})''\mathrm{O}$$

and no doubt similar derivatives will be formed from other glycols.*

3. If a mixture of hydrochloric and acetic acids be made to act on glycol, a body is produced which Simpson calls chloracetine of glycol.†

$$\underbrace{\left.\begin{matrix}\mathrm{H}\\(\mathrm{C_2H_4})''\\\mathrm{H}\end{matrix}\right\}\mathrm{O_2}}_{\text{Glycol.}} + \underbrace{\left.\begin{matrix}\mathrm{C_2H_3O}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}}_{\text{Acetic acid.}} = \underbrace{\left.\begin{matrix}\mathrm{C_2H_3O}\\(\mathrm{C_2H_4})''\\\mathrm{H}\end{matrix}\right\}\mathrm{O_2}}_{\text{Monacetate of glycol.}} + \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$$

$$\underbrace{\left.\begin{matrix}\mathrm{C_2H_3O}\\(\mathrm{C_2H_4})''\\\mathrm{H}\end{matrix}\right\}\mathrm{O_2}}_{\text{Monacetate of glycol.}} + \mathrm{HCl} = \underbrace{\left.\begin{matrix}\mathrm{C_2H_3O}\\(\mathrm{C_2H_4})''\end{matrix}\right\}\mathrm{O,Cl}}_{\text{Chloracetine of glycol.}} + \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$$

Chloracetine of glycol is a substance intermediate between Dutch liquid and diacetate of glycol. It is isomeric with chloracetine of ethylidine, which Simpson obtained by treating acetic aldehyde with chloride of acetyle.‡ It can be produced by passing a current of hydrochloric acid gas through monacetate of glycol at 100° C.

* Compt. rend. xlvii, 346; xlviii, 101; Ann. Ch. Pharm. cviii, 86, and cx, 126, 127; Chem. Gaz. vol. xvii, 155.

† Proc. R. S. ix, 726; x, 114. ‡ Compt. rend. Nov. 29, 1858.

Chloracetine of glycol and butyrate of silver, form butyroacetate of glycol.

$$\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\end{matrix}\right\}O,Cl + \left.\begin{matrix}C_4H_7O\\Ag\end{matrix}\right\}O = \left.\begin{matrix}C_2H_3O\\(C_2H_4)''\\C_4H_7O\end{matrix}\right\}O_2 + AgCl$$

Chloracetine of glycol. Butyroacetate of glycol.

If a stream of hydrochloric acid gas be passed through a mixture of equivalent quantities of butyric acid and glycol at 100°, chlorbutyrine of glycol if formed.

$$\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2 + \left.\begin{matrix}C_4H_7O\\H\end{matrix}\right\}O = \left.\begin{matrix}C_4H_7O\\(C_2H_4)''\\H\end{matrix}\right\}O_2 + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Monobutyrate of glycol.

$$\left.\begin{matrix}C_4H_7O\\(C_2H_4)''\\H\end{matrix}\right\}O_2 + HCl = \left.\begin{matrix}C_4H_7O\\(C_2H_4)''\end{matrix}\right\}O,Cl + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Chlorbutyrine of glycol.

In a similar way chlorbenzoate of glycol,

$$\left.\begin{matrix}C_7H_5O\\(C_2H_4)''\end{matrix}\right\}O,Cl$$

has been produced.

Iodacetine of glycol is formed by passing a current of hydriodic acid gas, through a mixture of equivalent quantities of glacial acetic acid and glycol. This compound can also be prepared with great facility, by exposing monacetate of glycol to the action of hydriodic acid gas.

$$\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\\H\end{matrix}\right\}O_2 + HI = \left.\begin{matrix}C_2H_3O\\(C_2H_4)''\end{matrix}\right\}O,I + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Iodacetine of glycol.

Chloracetine of glycol, chlorbutyrine of glycol, chlorbenzoate of glycol, iodhydrine of glycol, iodacetine of glycol as well as chlorhydrine of glycol are all decomposed by caustic potash, into oxide of ethylene, water and potash salts.

$$\underbrace{\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\end{matrix}\right\}O,Cl}_{\text{Chloracetine of glycol.}} + 2\left.\begin{matrix}K\\H\end{matrix}\right\}O = \underbrace{\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O}_{\text{Acetate of potash.}} + KCl$$

$$+ (C_2H_4)''O + H_2O$$

This process furnishes a convenient method of preparing oxide of ethylene, as the chloracetine can be obtained easily in large quantities. It is worthy of notice that in this reaction no glycol is reproduced; we also observe that bodies which yield oxide of ethylene in this manner with potash, are either glycol, in which one atom of hydrogen has been replaced by a monatomic acid radical, and the elements of peroxide of hydrogen by chlorine or iodine—or glycol in which only HO has been replaced by Cl or I.

$$\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2 \qquad \underbrace{\left.\begin{matrix}H\\(C_2H_4)''\end{matrix}\right\}O,Cl}_{\text{Chlorhydrine of glycol.}} \qquad \underbrace{\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\end{matrix}\right\}O,Cl}_{\text{Chloracetine of glycol.}}$$

On account of this decomposition with caustic potash, they might be regarded as compounds of oxide of ethylene with hydrochloric acid, chloride of acetyle, iodide of acetyle, &c.

4. Glycols produce with monatomic acids neutral compounds corresponding to the ethers of monatomic alcohols; with polyatomic acids, acid bodies analogous to sulphovinic acid. If from a polyatomic alcohol, one, two, or three atoms of peroxide of hydrogen be separated, the remaining part of the alcohol comports itself like a mono-, di-, or triatomic radical.

$$\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2 - HO = \left(\left.\begin{matrix}H\\(C_2H_4)''\end{matrix}\right\}O\right)' = (C_2H_5O)'$$

$$\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2 - 2HO = (C_2H_4)''$$

Under some conditions, glycol comports itself as if derived from one atom of water, and its composition may be represented by the formula

$$\left.\left(\frac{(C_2H_4)''}{H}\right\}O\right)'\Bigg\}O \quad \text{or} \quad \left.\begin{matrix}C_2H_5O\\H\end{matrix}\right\}O$$

If it be mixed with sulphuric acid and heated to 150° C., sulphoglycolic acid* is formed, which may be considered as sulphuric acid, wherein one atom of hydrogen is replaced by the atomic group C_2H_5O.

$$\left.\begin{matrix} H \\ (SO_2)'' \\ H \end{matrix}\right\} O_2 + \underbrace{\left.\begin{matrix} (C_2H_5O)' \\ H \end{matrix}\right\} O}_{\text{Glycol.}} = \underbrace{\left.\begin{matrix} (C_2H_5O)' \\ (SO_2)'' \\ H \end{matrix}\right\} O_2}_{\text{Sulphoglycolic acid.}} + \left.\begin{matrix} H \\ H \end{matrix}\right\} O$$

Sulphoglycolic acid appears to be monatomic.

The reactions of glycol with hydrogen and diatomic acids, may be conveniently expressed by adopting for glycol, the formula

$$(C_2H_4)''.\ (HO).\ HO$$

the diatomic radical C_2H_4, is here represented as combined with peroxide of hydrogen, which is monatomic. The formulæ of several compounds noticed, are accordingly;

$(C_2H_4)''(HO)$	Cl	Chlorhydrine of glycol.
$(C_2H_4)''Cl$	Cl	Dichloride of ethylene.
$(C_2H_4)''(HO)$	I	Iodhydrine of glycol.
$(C_2H_4)''I$	I	Diiodide of ethylene.
$(C_2H_4)''(C_2H_3O_2)$	Cl	Chloracetine of glycol.
$(C_2H_4)''(C_2H_3O_2)$	I	Iodacetine of glycol.
$(C_2H_4)''(C_4H_7O_2)$	Cl	Chlorbutyrine of glycol.
$(C_2H_4)''(C_7H_5O_2)$	Cl	Chlorbenzoate of glycol.

$$\left.\begin{matrix} \left((C_2H_4)''HO\right)' \\ (SO_2)'' \\ H \end{matrix}\right\} O_2$$ Sulphoglycolic acid.

The radicals $C_2H_3O_2$, $C_4H_7O_2$ and $C_7H_5O_2$, have the composition of the peroxides of the acid radicals of Mr. Brodie, and these peroxides would be the radicals of the monatomic oxygen-acids, if such acids be regarded as hydrogen-acids constructed on the type HCl. The above formulæ of glycol and several of its derivatives, are only meant to express the composition of these bodies in a more simple manner with regard to certain changes.

5. In contact with potassium or sodium, ethylo-glycol loses one

* Proc. R. S. ix, 725.

or two atoms of hydrogen, which are replaced by metal. The following two compounds have been prepared.

$$\left.\begin{matrix}\mathrm{Na}\\(\mathrm{C_2H_4})''\\\mathrm{H}\end{matrix}\right\}\mathrm{O_2} \qquad \left.\begin{matrix}\mathrm{Na}\\(\mathrm{C_2H_4})''\\\mathrm{Na}\end{matrix}\right\}\mathrm{O_2}$$

Propylo-, butylo-, and amylo-glycol comport themselves with potassium or sodium very probably in a similar manner.

Iodide of ethyl and $\left.\begin{matrix}\mathrm{Na}\\(\mathrm{C_2H_4})''\\\mathrm{H}\end{matrix}\right\}\mathrm{O_2}$ or $\left.\begin{matrix}\mathrm{Na}\\(\mathrm{C_2H_4})''\\\mathrm{Na}\end{matrix}\right\}\mathrm{O_2}$ decompose each other, and produce iodide of sodium and bodies which may be respectively considered as glycol, wherein one or both atoms of hydrogen are replaced by ethyl.

$$\left.\begin{matrix}\mathrm{Na}\\(\mathrm{C_2H_4})''\\\mathrm{H}\end{matrix}\right\}\mathrm{O_2} + \mathrm{C_2H_5I} = \left.\begin{matrix}\mathrm{C_2H_5}\\(\mathrm{C_2H_4})''\\\mathrm{H}\end{matrix}\right\}\mathrm{O_2} + \mathrm{NaI}$$

$$\left.\begin{matrix}\mathrm{Na}\\(\mathrm{C_2H_4})''\\\mathrm{Na}\end{matrix}\right\}\mathrm{O_2} + 2(\mathrm{C_2H_5I}) = \left.\begin{matrix}\mathrm{C_2H_5}\\(\mathrm{C_2H_4})''\\\mathrm{C_2H_5}\end{matrix}\right\}\mathrm{O_2} + 2\,\mathrm{NaI}$$

Monethylate of glycol, $\left.\begin{matrix}\mathrm{C_2H_5}\\(\mathrm{C_2H_4})''\\\mathrm{H}\end{matrix}\right\}\mathrm{O_2}$, in contact with potassium, loses hydrogen, and a compound is produced which may be considered as glycol, wherein one atom of hydrogen has been replaced by ethyl, the other by potassium.

$$\left.\begin{matrix}\mathrm{C_2H_5}\\(\mathrm{C_2H_4})''\\\mathrm{H}\end{matrix}\right\}\mathrm{O_2} + \mathrm{K} = \left.\begin{matrix}\mathrm{C_2H_5}\\(\mathrm{C_2H_4})''\\\mathrm{K}\end{matrix}\right\}\mathrm{O_2} + \mathrm{H}$$

Iodide of ethyl acts on $\left.\begin{matrix}\mathrm{C_2H_5}\\(\mathrm{C_2H_4})''\\\mathrm{K}\end{matrix}\right\}\mathrm{O_2}$ and produces iodide of potassium and diethyl-glycol.

$$\left.\begin{matrix}\mathrm{C_2H_5}\\(\mathrm{C_2H_4})''\\\mathrm{K}\end{matrix}\right\}\mathrm{O_2} + \mathrm{C_2H_5I} = \mathrm{KI} + \left.\begin{matrix}\mathrm{C_2H_5}\\(\mathrm{C_2H_4})''\\\mathrm{C_2H_5}\end{matrix}\right\}\mathrm{O_2}$$

The latter is isomeric with acetal.*

* Wurtz. Compt. rend. xlvii, 346; Ann. Ch. Pharm. cviii, 84.

6. Pentachloride of phosphorus and ethylo-glycol form hydrochloric acid, oxychloride of phosphorus and dichloride of ethylene.*

$$\left.\begin{matrix} H \\ (C_2H_4)'' \\ H \end{matrix}\right\} O_2 + \left.\begin{matrix} PCl_5 \\ PCl_5 \end{matrix}\right\} = (C_2H_4)''Cl_2 + 2\,HCl + 2\,POCl_3$$

7. Chloride of zinc abstracts water from ethylo- and propylo-glycol, and converts the one into acetic-, the other into propylic aldehyde.

$$\left.\begin{matrix} H \\ (C_2H_4)'' \\ H \end{matrix}\right\} O_2 - \left.\begin{matrix} H \\ H \end{matrix}\right\} O = \underset{\text{Acetic aldehyde.}}{C_2H_4O}$$

$$\left.\begin{matrix} H \\ (C_3H_6)'' \\ H \end{matrix}\right\} O_2 - \left.\begin{matrix} H \\ H \end{matrix}\right\} O = \underset{\text{Propylic aldehyde.}}{C_3H_6O}$$

8. In contact with air or oxygen, and platinum-black, the glycols oxidize with great rapidity. Nitric acid converts ethylo-glycol into glycolic, glyoxylic and oxalic acids. From propylo- and amylo-glycol, lactic and butylo-lactic acids have been obtained.†

$\underset{\text{Glycol.}}{C_2H_6O_2}$	$\underset{\text{Propylo-glycol.}}{C_3H_8O_2}$	$\underset{\text{Butylo-glycol.}}{C_4H_{10}O_2}$
$\underset{\text{Glycolic acid.}}{C_2H_4O_3}$	$\underset{\text{Lactic acid.}}{C_3H_6O_3}$	$\underset{\text{Butylo-lactic acid.}}{C_4H_8O_3}$

The acids contain two atoms of hydrogen less, and one atom of oxygen more, than their corresponding glycols. The same relation exists between the fatty acids and their alcohols. If in glycolic acid two atoms of hydrogen be replaced by one atom of oxygen, oxalic acid is formed. From lactic, and butylo-lactic acids, compounds homologous to oxalic acid will probably be obtained.

* Comp. rend. xlv, 228; Ann. Ch. Pharm. civ, 174.

† Compt. rend. xlv, 306; xliv. 1306; xlvi, 1232; Ann. Ch. Pharm. ciii, 366; cx, 316; cvii, 197; cv, 205; Chem. Gaz. xvii, 8; xvi, 441; xv, 341.

$C_2H_4O_3$	$C_3H_6O_3$	$C_4H_8O_3$
Glycolic acid.	Lactic acid.	Butylo-lactic acid.
$C_2H_2O_4$	$C_3H_4O_4$	$C_4H_6O_4$
Oxalic acid.	Malonic acid ?	Succinic acid ?

The composition of these acids and their corresponding glycols may also be expressed by the following formulæ.

(1.) $\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2$;	(4.) $\left.\begin{matrix}H\\(C_3H_6)''\\H\end{matrix}\right\}O_2$;	(7.) $\left.\begin{matrix}H\\(C_4H_8)''\\H\end{matrix}\right\}O_2$
Glycol.	Propylo-glycol.	Butylo-glycol.
(2.) $\left.\begin{matrix}H\\(C_2H_2O)''\\H\end{matrix}\right\}O_2$;	(5.) $\left.\begin{matrix}H\\(C_3H_4O)''\\H\end{matrix}\right\}O_2$;	(8.) $\left.\begin{matrix}H\\(C_4H_6O)''\\H\end{matrix}\right\}O_2$
Glycolic acid.	Lactic acid.	Butylo-lactic acid.
(3.) $\left.\begin{matrix}H\\(C_2O_2)''\\H\end{matrix}\right\}O_2$;	(6.) $\left.\begin{matrix}H\\(C_3H_2O_2)''\\H\end{matrix}\right\}O_2$;	(9.) $\left.\begin{matrix}H\\(C_4H_4O_2)''\\H\end{matrix}\right\}O_2$
Oxalic acid.	Malonic acid ?	Succinic acid ?

According to the formulæ 2, 5 and 8, glycolic-, lactic-, and butylo-lactic acids ought to be bibasic. Our present experience is very deficient on this point, and further experiments are required for its elucidation.

If glycol be oxidized by nitric acid, glyoxylic acid* is formed, together with glycolic and oxalic acids. Glyoxylic acid is an intermediate compound between glycolic and oxalic acids, just as oil of bitter almonds is intermediate between benzylic alcohol and benzoic acid.

C_7H_8O	$C_2H_4O_3$
Benzylic alcohol.	Glycolic acid.
C_7H_6O	$C_2H_2O_3$
Oil of bitter almonds.	Glyoxylic acid.
$C_7H_6O_2$	$C_2H_2O_4$
Benzoic acid.	Oxalic acid.

And as oil of bitter almonds and solution of potash decompose each other and produce benzylic alcohol and benzoate of potash, so the same alkali with glyoxylic acid forms glycolate and oxalate

* "On the action of nitric acid on alcohol." Phil. Mag., Nov., 1856.

of potash; and as oil of bitter almonds oxidizes with great ease and yields benzoic acid, so glyoxylic acid takes up oxygen readily, and becomes converted into oxalic acid.

$$2C_7H_6O + H_2O = \underbrace{C_7H_8O}_{\text{Benzylic alcohol.}} + \underbrace{C_7H_6O_2}_{\text{Benzoic acid.}}$$

$$2C_2H_2O_3 + H_2O = \underbrace{C_2H_4O_3}_{\text{Glycolic acid.}} + \underbrace{C_2H_2O_4}_{\text{Oxalic acid.}}$$

These acids combine with the potash present.

$$\underbrace{C_7H_6O}_{\text{Oil of bitter almonds.}} + O = \underbrace{C_7H_6O_2}_{\text{Benzoic acid.}}$$

$$\underbrace{C_2H_2O_3}_{\text{Glyoxylic acid.}} + O = \underbrace{C_2H_2O_4}_{\text{Oxalic acid.}}$$

A substance between glycol and glycolic acid, or glycol and oxalic acid, has not yet been obtained from glycol. But from ethylic alcohol, by oxidizing it with nitric acid, a body of the composition $C_2H_2O_2$ has been obtained. This body combines with bisulphite of ammonia and soda; acts on ammonia like oil of bitter almonds; yields, like acetic aldehyde, sulphur-compounds with sulphuretted hydrogen; and is easily oxidized by nitric acid into glyoxylic and oxalic acids, two substances which are also produced by the oxidation of glycol; $C_2H_2O_2$ seems to be a true aldehyde to glycol and oxalic acid.

$$\underbrace{C_2H_6O_2}_{\text{Glycol.}} = \left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\} O_2 \; ; \; \underbrace{C_2H_6O}_{\text{Alcohol.}} = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\} O$$

$$\underbrace{C_2H_2O_2}_{\text{Glyoxal.}} = \left.\begin{matrix}H\\(C_2\,.)''\\H\end{matrix}\right\} O_2 \quad \underbrace{C_2H_4O}_{\text{Aldehyde.}} = \left.\begin{matrix}C_2H_3\\H\end{matrix}\right\} O$$

$$\underbrace{C_2H_2O_4}_{\text{Oxalic acid.}} = \left.\begin{matrix}H\\(C_2O_2)''\\H\end{matrix}\right\} O_2 \; ; \; \underbrace{C_2H_4O_2}_{\text{Acetic acid.}} = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\} O$$

$$\underbrace{\left.\begin{matrix}H\\(C_2\cdot)''\\H\end{matrix}\right\}O_2}_{\text{Glyoxal.}} + O = \underbrace{\left.\begin{matrix}H\\(C_2O)''\\H\end{matrix}\right\}O_2}_{\text{Glyoxylic acid.}}$$

$$\underbrace{\left.\begin{matrix}H\\(C_2\cdot)''\\H\end{matrix}\right\}O_2}_{\text{Glyoxal.}} + 2O = \underbrace{\left.\begin{matrix}H\\(C_2O_2)''\\H\end{matrix}\right\}O_2}_{\text{Oxalic acid.}}$$

B. Compounds of the aldehydes $C_nH_{2n}O$ and $C_nH_{2n-8}O$.

a. *Acetic aldehyde.*

Acetic aldehyde is, as has already been stated, isomeric with oxide of ethylene. From aldehyde a series of bodies can be prepared isomeric with several glycol-compounds, and their composition is, as if they were derived from a diatomic alcohol of the formula,

$$\left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2.$$

With regard to these compounds, aldehyde may be represented as the oxide of the diatomic radical C_2H_4, *ethylidine*, isomeric, but not identical, with ethylene.

1. Acetic aldehyde and pentabromide of phosphorus form bromide of ethylidine and oxybromide of phosphorus.*

$$\underbrace{(C_2H_4)''O}_{\text{Aldehyde.}} + PBr_2,Br_3 = \underbrace{(C_2H_4)''Br_2}_{\text{Bromide of ethylidine.}} + POBr_3$$

Pentachloride of phosphorus and aldehyde decompose each other in a similar manner.

$$(C_2H_4)''O + PCl_2,Cl_3 = \underbrace{(C_2H_4)''Cl_2}_{\text{Chloride of ethylidine.}} + POCl_3$$

Chloride of ethylidine,† which is isomeric only with chloride of

* Wurtz & Frapolli. Compt. rend. xlvii, 418; Ann. Ch. Pharm. cviii, 225.
† Ann. Ch. Pharm. cv, 323.

ethylene, is decomposed by caustic potash into chloride of vinyle and hydrochloric acid, the same products of decomposition which are obtained under similar conditions from chloride of ethylene.

2. Hydrochloric acid and aldehyde form water and oxychloride of ethylidine.*

$$\begin{matrix}(C_2H_4)''O \\ (C_2H_4)''O\end{matrix} + \begin{matrix}HCl \\ HCl\end{matrix} = \underbrace{\left.\begin{matrix}(C_2H_4)'' \\ (C_2H_4)''\end{matrix}\right\} \begin{matrix}O \\ Cl_2\end{matrix}}_{\text{Oxychloride of ethylidine.}} + \left.\begin{matrix}H \\ H\end{matrix}\right\} O$$

Oxychloride of ethylidine is decomposed by water into aldehyde and hydrochloric acid: it is isomeric with chloretheral.

3. Chloride of acetyle and aldehyde combine and form

$$\left.\begin{matrix}(C_2H_4)'' \\ C_2H_3O\end{matrix}\right\} \begin{matrix}O\dagger \\ Cl\end{matrix}$$

This body is also produced by the action of chlorine on aldehyde. With solution of potash it forms aldehyde, chloride of potassium, and acetate of potash.

4. If acetic aldehyde and anhydrous acetic acid be heated in a sealed tube to 180°C. both unite and form

$$\left.\begin{matrix}(C_2H_4)'' \\ C_2H_3O \\ C_2H_3O\end{matrix}\right\} O_2 = \text{Acetate of aldehyde}\ddagger$$

which boils at 168°C. and is isomeric with diacetate of glycol. Hydrate of potash decomposes this compound, acetate of potash and aldehyde being produced.

5. Bromide of ethylidine and $\left.\begin{matrix}C_2H_5 \\ Na\end{matrix}\right\} O$ form bromide of sodium and acetal.

$$(C_2H_4)''Br_2 + 2\left.\begin{matrix}C_2H_5 \\ Na\end{matrix}\right\} O = 2NaBr + \underbrace{\left.\begin{matrix}C_2H_5 \\ (C_2H_4)'' \\ C_2H_5\end{matrix}\right\} O_2}_{\text{Acetal.}}$$

* Compt. rend. xlvi, 662; Ann. Ch. Pharm. cvi, 336.

† Compt. rend. xlvii, 874; Ann Ch. Pharm. cix, 156.

‡ Geuther. Ann. Ch. Pharm. cvi, 249.

Ethylic alcohol, acetic aldehyde, and hydrochloric acid produce a liquid which boils at 95°C. and has the formula

$$\begin{matrix}(C_2H_4)''\\ C_2H_5\end{matrix}\Big\}\ O\ \Big\}\ Cl$$

$$\begin{matrix}C_2H_5\\ H\end{matrix}\Big\}\ O \ + \ HCl \ = \ \begin{matrix}H\\ H\end{matrix}\Big\}\ O \ + \ C_2H_5Cl$$

$$(C_2H_4)''O \ + \ C_2H_5Cl \ = \ \begin{matrix}(C_2H_4)''\\ C_2H_5\end{matrix}\Big\}\ O\ \Big\}\ Cl$$

This compound is decomposed by ethylate of sodium acetal and chloride of sodium being formed.

$$\begin{matrix}(C_2H_4)''\\ C_2H_5\end{matrix}\Big\}\ O\ \Big\}\ Cl \ + \ \begin{matrix}C_2H_5\\ Na\end{matrix}\Big\}\ O \ = \ \left.\begin{matrix}C_2H_5\\ (C_2H_4)''\\ C_2H_5\end{matrix}\right\}\ O_2 \ + \ NaCl$$

Acetal, which is isomeric with diethyl-glycol, is also formed by the oxidation of ethylic alcohol. If hydrochloric acid acts on acetal, chloride of ethyl occurs amongst the products of decomposition.

When chlorine acts on ethylic alcohol, the following substances are obtained.

$C_6H_{13}Cl\,O_2$ = Monochlorinated acetal.
$C_6H_{12}Cl_2O_2$ = Bichlorinated acetal.
$C_6H_{11}Cl_3O_2$ = Trichlorinated acetal.

Chloral stands to trichlorinated acetal as aldehyde does to acetal.

6. If a mixture of sulphuric acid, water, peroxide of manganese, and ethylic and methylic alcohols be distilled, the following two compounds are obtained.

$$\left.\begin{matrix}(C_2H_4)''\\ C\ H_3\\ C\ H_3\end{matrix}\right\}\ O_2$$

$$\left.\begin{matrix}(C_2H_4)''\\ C\ H_3\\ C_2H_5\end{matrix}\right\}\ O_2$$

Acetal wherein one or both atoms of ethyl have been replaced by methyl.

The following is a list of those compounds, derived from glycol and acetic aldehyde, which are isomeric.

Aldehyde	C_2H_4O	Oxide of ethylene	C_2H_4O
Chloride of ethylidine	$(C_2H_4)''Cl_2$	Chloride of ethylene	$(C_2H_4)''Cl_2$
Chloracetine of ethylidine	$\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\end{matrix}\right\}$ O,Cl	Chloracetine of glycol	$\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\end{matrix}\right\}$ O,Cl
Acetate of aldehyde	$\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\\C_2H_3O\end{matrix}\right\}$ O_2	Diacetate of glycol	$\left.\begin{matrix}C_2H_3O\\(C_2H_4)''\\C_2H_3O\end{matrix}\right\}$ O_2
Acetal	$\left.\begin{matrix}C_2H_5\\(C_2H_4)''\\C_2H_5\end{matrix}\right\}$ O_2	Diethylo-glycol	$\left.\begin{matrix}C_2H_5\\(C_2H_4)''\\C_2H_5\end{matrix}\right\}$ O_2

b. *Valerianic aldehyde.*

The aldehyde of valerianic acid has also been combined with acetic and benzoic acids.

Acetic acid compound	$\left.\begin{matrix}C_2H_3O\\C_2H_3O\\(C_5H_{10})''\end{matrix}\right\}$ O_2	Benzoic acid compound	$\left.\begin{matrix}C_7H_5O\\C_7H_5O\\(C_5H_{10})''\end{matrix}\right\}$ O_2

These compounds are respectively decomposed by caustic potash into valerianic aldehyde, and acetate and benzoate of potash.* Acetate of valerianic aldehyde is isomeric with diacetate of amylo-glycol.

c. *Benzoic aldehyde.*

Pentachloride of phosphorus and oil of bitter almonds form oxychloride of phosphorus and chlorobenzole.

$$\underset{\text{Oil of bitter almonds.}}{(C_7H_6)''O} + PCl_5 = \underset{\text{Chlorobenzole.}}{(C_7H_6)''Cl_2} + POCl_3$$

* Guthrie and Kolbe. Ann. Ch. Pharm. cix, 298.

If chlorobenzole be placed in contact with $\left.\begin{matrix}CH_3\\Na\end{matrix}\right\}O$, chloride of sodium and $\left.\begin{matrix}(C_7H_6)''\\C\,H_3\\C\,H_3\end{matrix}\right\}O_2$ are produced.

$$(C_7H_6)''Cl_2 + 2\left.\begin{matrix}CH_3\\Na\end{matrix}\right\}O = 2NaCl + \left.\begin{matrix}(C_7H_6)''\\C\,H_3\\C\,H_3\end{matrix}\right\}O_2$$

In a similar manner we obtain

$\left.\begin{matrix}(C_7H_6)''\\C_2H_5\\C_2H_5\end{matrix}\right\}O_2$ from ethylate of sodium

$\left.\begin{matrix}(C_7H_6)''\\C_5H_{11}\\C_5H_{11}\end{matrix}\right\}O_2$ from amylate of sodium

$\left.\begin{matrix}(C_7H_6)''\\C_2H_3O\\C_2H_3O\end{matrix}\right\}O_2$, acetate of benzole, from acetate of silver and chlorobenzole, and

$\left.\begin{matrix}(C_7H_6)''\\C_7H_5O\\C_7H_5O\end{matrix}\right\}O_2$, benzoate of benzole, from benzoate of silver and chlorobenzole

Acetate, benzoate, and chloride of benzole can be decomposed with caustic potash, acetate and benzoate of potash and chloride of potassium, together with oil of bitter almonds, being respectively formed; a corresponding alcohol of the formula $\left.\begin{matrix}C_7H_6\\H_2\end{matrix}\right\}O_2$ could not be obtained.*

With regard to these compounds, oil of bitter almonds may be regarded as the oxide of the diatomic radical $(C_7H_6)''$.

d. *Cuminic Aldehyde.*

Chlorocumole and benzoate of silver yield chloride of silver and benzoate of cumole.†

* Ann. Ch. Pharm. cii, 356, 373.

† Ann. Ch. Pharm., cvi, 258; cix, 367. Petersb. Acad. Bull. xvii, 125.

$$(C_{10}H_{12})''Cl_2 + \left.\begin{matrix}C_7H_5O\\Ag\\C_7H_5O\\Ag\end{matrix}\right\} O_2 = 2AgCl + \left.\begin{matrix}C_7H_5O\\(C_{10}H_{12})''\\C_7H_5O\end{matrix}\right\} O_2$$

Acetate of cumole has also been prepared from acetate of silver and chloride of cumole.

$$\left.\begin{matrix}C_2H_3O\\(C_{10}H_{12})''\\C_2H_3O\end{matrix}\right\} O_2$$

Caustic potash decomposes these bodies in a manner analogous to that in which it decomposes the benzole compounds.

Meconine and saligenine may perhaps be added to the diatomic alcohols. Berthelot obtained

Stearo-meconine $\left.\begin{matrix}(C_{10}H_8O_2)''\\C_{18}H_{35}O\\C_{18}H_{35}O\end{matrix}\right\} O_2$

Saligenine appears to be the alcohol of salicylous and salicylic acids. Salicylous acid is produced from saligenine by oxidation with chromic acid, as aldehyde and acetic acid are from ethylic alcohol. Benzole-alcohol, $\left.\begin{matrix}(C_7H_6)''\\H_2\end{matrix}\right\} O_2$, derived from chlorobenzole, $(C_7H_6)''Cl_2$, will be, if it at all exist, isomeric with saligenine.

Saligenine $\left.\begin{matrix}(C_7H_6)''\\H_2\end{matrix}\right\} O_2$

Saliretine, formed by the action of sulphuric acid on saligenine, is perhaps the ether of saligenine.

Saliretine $\left.\begin{matrix}(C_7H_6)''\\(C_7H_6)''\end{matrix}\right\} O_2$

Salicine may be represented as saligenine wherein one atom of hydrogen has been replaced by $C_6H_{11}O_5$

Salicine $\left.\begin{matrix}(C_7H_6)''\\C_6H_{11}O_5\\H\end{matrix}\right\} O_2$

and populine as saligenine wherein one atom of hydrogen has been replaced by benzoyle, C_7H_5O and another by $C_6H_{11}O_5$.

Populine $\left.\begin{matrix}(C_7H_6)''\\C_7H_5O\\C_6H_{11}O_5\end{matrix}\right\} O_2 + 2H_2O$

Very little is known of the alcohol of anisic acid, $C_8H_{10}O_2$.*

C. *Triatomic Alcohols.*

Glycerine

represents three atoms of water, wherein three atoms of hydrogen have been replaced by the triatomic radical $(C_3H_5)'''$.

$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\} O_3$ $\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\} O_3$, Glycerine.

1. This substance combines with monatomic acids with elimination of water, and produces neutral compounds which, by respective treatment with caustic potash or soda, hydrochloric and acetic acids and water, are decomposed into glycerine and acid. As one, two or three atoms of hydrogen can be replaced in glycerine, three compounds may be formed from glycerine and the same acid.

$$\underbrace{\left.\begin{matrix}(C_3H_5)'''\\H\\H\\H\end{matrix}\right\} O_3}_{\text{Glycerine.}} + \underbrace{\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\} O}_{\text{Acetic acid.}} = \underbrace{\left.\begin{matrix}(C_3H_5)'''\\H\\H\\C_2H_3O\end{matrix}\right\} O_3}_{\text{Acetine.}} + \left.\begin{matrix}H\\H\end{matrix}\right\} O$$

$$\underbrace{\left.\begin{matrix}(C_3H_5)'''\\H\\H\\H\end{matrix}\right\} O_3}_{\text{Glycerine.}} + \underbrace{2\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\} O}_{\text{Acetic acid.}} = \underbrace{\left.\begin{matrix}(C_3H_5)'''\\H\\C_2H_3O\\C_2H_3O\end{matrix}\right\} O_3}_{\text{Diacetine.}} + 2\left.\begin{matrix}H\\H\end{matrix}\right\} O$$

$$\underbrace{\left.\begin{matrix}(C_3H_5)'''\\H\\H\\H\end{matrix}\right\} O_3}_{\text{Glycerine.}} + \underbrace{3\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\} O}_{\text{Acetic acid.}} = \underbrace{\left.\begin{matrix}(C_3H_5)'''\\C_2H_3O\\C_2H_3O\\C_2H_3O\end{matrix}\right\} O_2}_{\text{Triacetine.}} + 3\left.\begin{matrix}H\\H\end{matrix}\right\} O$$

These bodies are obtained by heating mixtures of glycerine and

* Cannizaro and Bertagnini, Cimento i, 99; Ann. Ch. Pharm. xcviii, 188. Liebig and Kopp's Jahresbericht, (1855) 623.

acid in sealed tubes at temperatures varying from 100° to 300° C. for several hours. According to temperature, pressure, and the relative quantity of materials employed, one, two, or three atoms of hydrogen are replaced in glycerine by acid radicals. The product is treated with slaked lime or carbonate of soda, in order to remove the uncombined acid, and digested with ether. The compound is left as a residue when the ethereal solution is evaporated. The glycerides, as these compounds may be called, of the volatile fatty acids are oily liquids; stearine and palmitine are solids; only few are volatile without decomposition.

The following is a list of those compounds which contain a monatomic acid or basic radical that have already been prepared.*

Monoglycerides.

$\left.\begin{matrix}(C_3H_5)'''\\H\\H\\H\end{matrix}\right\}O_3$ Glycerine.

$\left.\begin{matrix}(C_3H_5)'''\\H\\H\\C_2H_3O\end{matrix}\right\}O_3$ Acetine.

$\left.\begin{matrix}(C_3H_5)'''\\H\\H\\C_4H_7O\end{matrix}\right\}O_3$ Monobutyrine.

$\left.\begin{matrix}(C_3H_5)'''\\H\\H\\C_5H_9O\end{matrix}\right\}O_3$ Monovalerine.

$\left.\begin{matrix}(C_3H_5)'''\\H\\H\\C_{16}H_{31}O\end{matrix}\right\}O_3$ Monopalmitine.

$\left.\begin{matrix}(C_3H_5)'''\\H\\H\\C_{18}H_{35}O\end{matrix}\right\}O_3$ Monostearine.

$\left.\begin{matrix}(C_3H_5)'''\\H\\H\\C_{18}H_{33}O\end{matrix}\right\}O_3$ Monoleine.

$\left.\begin{matrix}(C_3H_5)'''\\H\\H\\C_7H_5O\end{matrix}\right\}O_3$ Benzoycine.

Diglycerides.

$\left.\begin{matrix}(C_3H_5)'''\\H\\C_2H_3O\\C_2H_3O\end{matrix}\right\}O_3$ Diacetine.

$\left.\begin{matrix}(C_3H_5)'''\\H\\C_4H_7O\\C_4H_7O\end{matrix}\right\}O_3$ Dibutyrine.

* Compt. rend. xxxvii, 398; xxxviii, 668; Ann. Ch. Pharm. lxxxviii, 304; xcii, 301, 305; Chem. Soc. Qu. J. vi, 280; vii, 222. Chem. Gaz. (1853) 421; (1854) 340. Jahresbericht, (1853) 451; (1854) 448; Ann. Ch. Phys. [3] xli, 216; Proc. R. S. vii, 130.

$$\left.\begin{matrix}(C_3H_5)'''\\ H\\ C_5H_9O\\ C_5H_9O\end{matrix}\right\}O_3$$ Divalerine.

$$\left.\begin{matrix}(C_3H_5)'''\\ H\\ C_{18}H_{35}O\\ C_{18}H_{35}O\end{matrix}\right\}O_3$$ Distearine.

$$\left.\begin{matrix}(C_3H_5)'''\\ H\\ C_{16}H_{31}O\\ C_{16}H_{31}O\end{matrix}\right\}O_3$$ Dipalmitine.

$$\left.\begin{matrix}(C_3H_5)'''\\ H\\ C_{18}H_{33}O\\ C_{18}H_{33}O\end{matrix}\right\}O_3$$ Dioleine.

$$\left.\begin{matrix}(C_3H_5)'''\\ H\\ C_2H_5\\ C_2H_5\end{matrix}\right\}O_3$$ Diethyline.

Berthelot considers divalerine, dipalmitine, distearine, and dioleine to contain one atom of water more than represented by the above formulæ.

Triglycerides.

$$\left.\begin{matrix}(C_3H_5)'''\\ NO_2\\ NO_2\\ NO_2\end{matrix}\right\}O_3$$ Nitroglycerine.

$$\left.\begin{matrix}(C_3H_5)'''\\ C_{16}H_{31}O\\ C_{16}H_{31}O\\ C_{16}H_{31}O\end{matrix}\right\}O_3$$ Tripalmitine.

$$\left.\begin{matrix}(C_3H_5)'''\\ C_2H_3O\\ C_2H_3O\\ C_2H_3O\end{matrix}\right\}O_3$$ Triacetine.

$$\left.\begin{matrix}(C_3H_5)'''\\ C_{18}H_{35}O\\ C_{18}H_{35}O\\ C_{18}H_{35}O\end{matrix}\right\}O_3$$ Tristearine; identical with the stearine of fats.

$$\left.\begin{matrix}(C_3H_5)'''\\ C_4H_7O\\ C_4H_7O\\ C_4H_7O\end{matrix}\right\}O_3$$ Tributyrine.

$$\left.\begin{matrix}(C_3H_5)'''\\ C_{18}H_{33}O\\ C_{18}H_{33}O\\ C_{18}H_{33}O\end{matrix}\right\}O_3$$ Trioleine.

$$\left.\begin{matrix}(C_3H_5)'''\\ C_5H_9O\\ C_5H_9O\\ C_5H_9O\end{matrix}\right\}O_3$$ Trivalerine.

$$\left.\begin{matrix}(C_3H_5)'''\\ C_7H_5O\\ C_7H_5O\\ C_7H_5O\end{matrix}\right\}O_3$$ Tribenzoycine.

Some of these compounds, as monostearine, diethyline, distearine, tribenzoycine, &c., crystallize. Chevreul, Pelouze and Gélis, Duffy, Heintz, and especially Berthelot, have furnished important researches on the glycerides. According to the method which the latter chemist employed, it seems that some of the compounds obtained by him were not quite pure, and the analy-

tical results bear out this supposition. But considering the general chemical comportment of glycerine, the formulæ given in the above list are most probably a correct representation of the composition of these compounds.

2. The compounds, produced by the action of sulphuric, tartaric, and phosphoric acids on glycerine, possess an acid character; combine with bases; decompose very easily into glycerine and acid by treatment with water; and may be compared to sulphovinic acid. If the latter be considered as sulphuric acid wherein one atom of hydrogen has been replaced by ethyl, then the corresponding compound of glycerine may be represented as sulphuric acid wherein one atom of hydrogen has been replaced by the monatomic radical $C_3H_7O_2$, derived from glycerine. The same remark applies equally to tartro- and phospho-glyceric acids.

Sulphoglyceric acid* is formed by mixing one part of glycerine with two parts of sulphuric acid.

$$\left.\begin{matrix}C_3H_7O_2\\H\end{matrix}\right\}O + \left.\begin{matrix}SO_2\\H\\H\end{matrix}\right\}O_2 = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}SO_2\\C_3H_7O_2\\H\end{matrix}\right\}O_2$$

Glycerine. Sulphoglyceric acid.

Sulphoglyceric acid is monobasic; the following salts are known:—

$$\left.\begin{matrix}C_3H_7O_2\\SO_2\\Ba\end{matrix}\right\}O_2$$ Sulphoglycerate of baryta.

$$\left.\begin{matrix}C_3H_7O_2\\SO_2\\Ca\end{matrix}\right\}O_2$$ Sulphoglycerate of lime.

$$\left.\begin{matrix}C_3H_7O_2\\SO_2\\Pb\end{matrix}\right\}O_2$$ Sulphoglycerate of lead.

Tartroglyceric acid is formed by heating equivalent quantities of glycerine and tartaric acid to 150° C.

$$\left.\begin{matrix}C_3H_7O_2\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\(C_4H_4O_4)''\\H\end{matrix}\right\}O_2 = \left.\begin{matrix}C_3H_7O_2\\(C_4H_4O_4)''\\H\end{matrix}\right\}O_2 + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Glycerine. Tartaric acid. Tartroglyceric acid.

* Pelouze. (1836.) Ann. Ch. Phys. lxiii, 21; Ann. Ch. Pharm. Liebig & Wöhler. xix, 211.

It appears that only the lime-salt of this acid is known.

$$\left.\begin{matrix} C_3H_7O_2 \\ (C_4H_4O_4)'' \\ Ca \end{matrix}\right\} O_2 \text{ Tartroglycerate of lime.}$$

Phosphoglyceric acid* is formed by mixing glycerine with solid phosphoric acid

$$\underbrace{\left.\begin{matrix} C_3H_7O_2 \\ H \end{matrix}\right\} O}_{\text{Glycerine.}} + \left.\begin{matrix} (PO)''' \\ H \\ H \\ H \end{matrix}\right\} O_3 = \underbrace{\left.\begin{matrix} (PO)''' \\ C_3H_7O_2 \\ H \\ H \end{matrix}\right\} O_3}_{\text{Phosphoglyceric acid.}} + \left.\begin{matrix} H \\ H \end{matrix}\right\} O$$

A compound of this acid is supposed to exist in the yolk of eggs and in the brain; it is dibasic, and has furnished the following salts:—

$$\left.\begin{matrix} (PO)''' \\ C_3H_7O_2 \\ Ba \\ Ba \end{matrix}\right\} O_3 \text{ Phosphoglycerate of baryta.}$$

$$\left.\begin{matrix} (PO)''' \\ C_3H_7O_2 \\ Ca \\ Ca \end{matrix}\right\} O_3 \text{ Phosphoglycerate of lime.}$$

$$\left.\begin{matrix} (PO)''' \\ C_3H_7O_2 \\ Pb \\ Pb \end{matrix}\right\} O_3 \text{ Phosphoglycerate of lead.}$$

Sebacine, being a derivative from glycerine and a bibasic acid, has to be mentioned.

$$\underbrace{2\left(\left.\begin{matrix} C_3H_7O_2 \\ H \end{matrix}\right\} O\right)}_{\text{Glycerine.}} + \underbrace{\left.\begin{matrix} H \\ (C_{10}H_{16}O_2)'' \\ H \end{matrix}\right\} O_2}_{\text{Sebacic acid.}} = \underbrace{\left.\begin{matrix} C_3H_7O_2 \\ (C_{10}H_{16}O_2)'' \\ C_3H_7O_2 \end{matrix}\right\} O_2}_{\text{Sebacine.}} + 2\left.\begin{matrix} H \\ H \end{matrix}\right\} O$$

Sebacine is neutral, and is decomposed by oxide of lead into glycerine, and a lead-salt of sebacic acid.

* Compt. rend. xxi, 718; Gobley. J. Pharm. [3] ix, 161; xi, 409; xii, 5.

Van Bemmelen* obtained succinine, benzosuccinine, and citro-glycerine by heating glycerine to 220° C. with succinic acid, with a mixture of benzoic and succinic acids, and with citric acid. These substances are insoluble in water, alcohol, ether, and bisulphide of carbon; their formulæ, which Van Bemmelen attributes to them, are subjoined, but no great reliance can be placed on their correctness.

$$\left.\begin{matrix}(C_3H_5)''' \\ H \\ C_4H_4O_2)''\end{matrix}\right\} O_3 \text{ Succinine.}$$

$$\left.\begin{matrix}(C_3H_5)''' \\ C_7H_5O \\ (C_4H_4O_2)''\end{matrix}\right\} O_3 \text{ Benzosuccinine.}$$

$$\left.\begin{matrix}(C_3H_5)''' \\ (C_6H_5O_4)'''\end{matrix}\right\} O_3 \text{ Citroglycerine.}$$

3. If glycerine, saturated with hydrochloric acid gas, be heated in a sealed tube to 100° C. for several hours, chlorhydrine and dichlorhydrine are formed.†

$$\underbrace{\left.\begin{matrix}(C_3H_5)''' \\ H_3\end{matrix}\right\} O_3}_{\text{Glycerine.}} + HCl = \underbrace{\left.\begin{matrix}(C_3H_5)''' \\ H_2\end{matrix}\right\} O_2,Cl}_{\text{Monochlorhydrine.}} + H_2O$$

$$\underbrace{\left.\begin{matrix}(C_3H_5)''' \\ H_3\end{matrix}\right\} O_3}_{\text{Glycerine.}} + 2HCl = \underbrace{\left.\begin{matrix}(C_3H_5)''' \\ H\end{matrix}\right\} O,Cl_2}_{\text{Dichlorhydrine.}} + 2H_2O$$

Dichlorhydrine and hydrochloric acid at 100° C. produce epichlorhydrine.

$$\underbrace{\left.\begin{matrix}(C_3H_5)''' \\ H\end{matrix}\right\} O,Cl_2}_{\text{Dichlorhydrine.}} - HCl = \underbrace{\left.\begin{matrix}(C_3H_5)''' \end{matrix}\right\} O'Cl}_{\text{Epichlorhydrine.}}$$

When dichlorhydrine changes to epichlorhydrine, the radical $(C_3H_5)'''$ perhaps loses one atom of hydrogen, and is converted into the diatomic radical $(C_3H_4)''$. In this case, the formula of epichlorhydrine would be $\left.\begin{matrix}(C_3H_4)'' \\ H\end{matrix}\right\} O,Cl$.

* Liebig and Kopp's Jahresber. (1856). 602.

† Ann. Chim. et de Phys. (3.) xli. 216; Ann. Ch. Pharm. xcii, 302; lxxxviii, 311; Liebig, Jahresbericht. (1854), 449; (1853), 455.

Chlorhydrine boils at 227° C., dichlorhydrine at 178° C., and epichlorhydrine at about 120° C. Chlorhydrine and dichlorhydrine regenerate glycerine by treatment with oxide of lead or potash.

4. On heating glycerine saturated with hydriodic acid, to 100° C. for forty hours, iodhydrine is generated.*

$$2\left(\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3\Big) + HI = \underbrace{C_6H_{11}IO_3}_{\text{Iodhydrine.}} + 3H_2O$$

Iodhydrine is not volatile without decomposition; when treated with potash, it yields iodide of potassium, a substance resembling glycerine and a body, $C_6H_{10}O_3$, which is probably the ether of glycerine.

Glycerine $\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3$ Oxide of glyceryle $\left.\begin{matrix}(C_3H_5)'''\\(C_3H_5)'''\end{matrix}\right\}O_3$

5. The chlorides of phosphorus and glycerine produce the same substances which are obtained by acting with hydrochloric acid on glycerine; monochlorhydrine, dichlorhydrine, and epichlorhydrine, as well as small quantities of trichlorhydrine and epidichlorhydrine are formed. The last two substances are formed abundantly by the action of PCl_5 on dichlorhydrine.†

$$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3 + PCl_5 = \underbrace{\left.\begin{matrix}(C_3H_5)'''\\H_2\end{matrix}\right\}O_2Cl}_{\text{Monochlorhydrine.}} + HCl + PCl_3O$$

$$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3 + 2PCl_5 = \underbrace{\left.\begin{matrix}(C_3H_5)'''\\H\end{matrix}\right\}O,Cl_2}_{\text{Dichlorhydrine.}} + 2HCl + 2PCl_3O$$

$$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3 + PCl_3O = \underbrace{(C_3H_5)''',Cl_3}_{\text{Trichlorhydrine.}} + PH_3O_4$$

$$\underbrace{\left.\begin{matrix}(C_3H_5)'''\\H\end{matrix}\right\}O,Cl_2}_{\text{Dichlorhydrine.}} - HCl = \underbrace{\left.\begin{matrix}(C_3H_4)''\\H\end{matrix}\right\}O,Cl}_{\text{Epichlorhydrine.}}$$

$$\underbrace{(C_3H_5)'''Cl_3}_{\text{Trichlorhydrine.}} - HCl = \underbrace{(C_3H_4)'', Cl_2}_{\text{Epidichlorhydrine.}}$$

* Compt. rend. xxxix, 748; Ann. Ch. Phys. (3) xliii, 279; Ann. Ch. Pharm. xcii, 311; Jahresbericht von Liebig & Kopp, (1854), 453.

† Ann. Ch. Phys. (3), lii, 433; Jahresbericht von Liebig, (1857), 477.

Trichlorhydrine boils at about 155° C., and epidichlorhydrine at about 120° C.; both, if heated to 100° C. with moist oxide of silver, regenerate glycerine.

6. The derivatives from glycerine and the bromides of phosphorus are very numerous; monobromhydrine, dibromhydrine, tribromhydrine, epibromhydrine, hemibromhydrine, acroleine, and two compounds $C_{18}H_{27}BrO_7$ and $C_6H_9Br_2P$, have been obtained in a tolerably pure state.* Glycerine and terbromide of phosphorus act upon each other as follows:—

$$3\left(\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3\Big) + 2(PBr_3) = 3\Big(\underbrace{\left.\begin{matrix}(C_3H_5)'''\\H_2\end{matrix}\right\}O_2,Br}_{\text{Monobromhydrine.}}\Big) + 3HBr + P_2O_3$$

$$3\Big(\underbrace{\left.\begin{matrix}(C_3H_5)'''\\H_2\end{matrix}\right\}O_2Br}_{\text{Monobromhydrine.}}\Big) + 2(PBr_3) = 3\Big(\underbrace{\left.\begin{matrix}(C_3H_5)'''\\H\end{matrix}\right\}OBr_2}_{\text{Dibromhydrine.}}\Big) + 3HBr + P_2O_3$$

The distillation of dibromhydrine with pentabromide of phosphorus yields tribromhydrine and a compound, $C_3H_7Br_3O$.

$$\underbrace{\left.\begin{matrix}(C_3H_5)'''\\H\end{matrix}\right\}O,Br_2}_{\text{Dibromhydrine.}} + PBr_5 = \underbrace{(C_3H_5)''',Br_3}_{\text{Tribromhydrine.}} + HBr + PBr_3O$$

$$\left.\begin{matrix}(C_3H_5)'''\\H\end{matrix}\right\}O,Br_2 + HBr = C_3H_7Br_3O$$

Epibromhydrine is obtained in large quantities by the action of liquid bromide of phosphorus on glycerine.

$$\underbrace{\left.\begin{matrix}(C_3H_5)'''\\H\end{matrix}\right\}O,Br_2}_{\text{Dibromhydrine.}} - HBr = \underbrace{\left.\begin{matrix}(C_3H_4)''\\H\end{matrix}\right\}O,Br}_{\text{Epibromhydrine.}} = (C_3H_5)''O''Br$$

Along with monobromhydrine, dibromhydrine, and epibromhydrine, Berthelot and Luca obtained three substances, the formulæ of which, according to these chemists, are $C_6H_9BrO_2$, $C_6H_9Br_2P$, and $C_{18}H_{27}BrO_7$.

* Ann Ch. Phys. (3) xlviii, 304; Ann. Ch. Pharm. ci, 68; Jahresbericht. von Liebig & Kopp, (1856), 599.

$$\underbrace{2\left(\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3\right)}_{\text{Glycerine,}} + HBr - 4H_2O = \underbrace{C_6H_9BrO_2}_{\text{Hemibromhydrine.}}$$

$$\underbrace{6\left(\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3\right)}_{\text{Glycerine.}} + HBr - 11H_2O = C_{18}H_{27}BrO_7$$

The two formulæ $C_6H_9BrO_2$ and $C_{18}H_{27}BrO_7$ seem to be not well established, and the substances which they represent require further investigation. $C_6H_9Br_2P$ will be considered with the nitrogen derivatives of glycerine.

The formation of acroleine, by the action of PBr_3 on glycerine, is easily understood.

$$C_3H_8O_3 - 2H_2O = \underbrace{C_3H_4O}_{\text{Acroleine.}}$$

The water which separates from the glycerine unites perhaps with the phosphorous acid, produced at the same time.

Monobromhydrine, dibromhydrine, epibromhydrine and hemibromhydrine, by treatment with potash, and tribromhydrine and $C_3H_7Br_3O$, by treatment with moist oxide of silver, regenerate glycerine. Dibromhydrine is the chief product obtained by the action of PBr_3 on glycerine. Epibromhydrine boils at 138° C.; dibromhydrine at 219° C.; hemibromhydrine below 200° C.; tribromhydrine at about 180° C.; and monobromhydrine in vacuo at about 180° C. These five substances are neutral liquids. Tribromhydrine $(C_3H_5)'''Br_3$, brominated bromide of propylene $(C_3H_5Br)'',Br_2$, and terbromide of allyle, obtained by the action of bromine on iodide of allyle, are isomeric, but not identical; only the first and last are able to furnish glycerine.

7. The action of iodide of phosphorus on glycerine is represented by the following equation.*

$$\underbrace{\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\Big\}O_3}_{\text{Glycerine.}} + PI_2 = \underbrace{(C_3H_5)',I}_{\text{Iodide of allyle.}} + \underbrace{PH_3O_3}_{\text{Phosphorous acid.}} + I$$

The teratomic radical glyceryle, $(C_3H_5)'''$, changes in this reaction and becomes converted into the monatomic radical, allyle. Besides iodide of allyle some propylene, C_3H_6, is formed, in consequence of a secondary reaction.

* Ann. Ch. Phys. (3) xliii, 257; Ann. Ch. Pharm. xcii, 306; Jahresbericht (1854), 451.

8. Compounds derived from glycerine with more than one acid, chloride or bromide, have next to be considered.* Dibromhydrine and pentachloride of phosphorus produce hydrochloric acid, oxychloride of phosphorus and chlorhydrodibromhydrine.

$$\underbrace{\left.\begin{matrix}(C_3H_5)'''\\ H\end{matrix}\right\} O,Br_2}_{\text{Dibromhydrine.}} + PCl_5 = \underbrace{(C_3H_5)''',Cl,Br_2}_{\text{Chlorhydrodibromhydrine.}} + PCl_3O + HCl$$

From dichlorhydrine and pentabromide of phosphorus, bromhydrodichlorhydrine is obtained.

$$\underbrace{\left.\begin{matrix}(C_3H_5)'''\\ H\end{matrix}\right\} O,Cl_2}_{\text{Dichlorhydrine.}} + PBr_5 = \underbrace{(C_3H_5)''',Br,Cl_2}_{\text{Bromhydrodichlorhydrine.}} + PBr_3O + HBr$$

Chlorhydrodibromhydrine and bromhydrodichlorhydrine are neutral liquids, which regenerate glycerine by treatment with moist oxide of silver.

Instead of chlorine or bromine, the atomic group $(C_2H_3O)'O$, derived from acetic acid, may be introduced into these substances.

Chloride of acetyle and glycerine form acetochlorhydrine, acetodichlorhydrine and water.

$$\underbrace{\left.\begin{matrix}(C_3H_5)'''\\ H_3\end{matrix}\right\} O_3}_{\text{Glycerine.}} + \underbrace{C_2H_3O,Cl}_{\text{Chloride of acetyle.}} = \underbrace{\left.\begin{matrix}(C_3H_5)'''\\ C_2H_3O\\ H\end{matrix}\right\} O_2,Cl}_{\text{Acetochlorhydrine.}} + H_2O$$

$$\underbrace{\left.\begin{matrix}(C_3H_5)'''\\ C_2H_3O\\ H\end{matrix}\right\} O_2Cl}_{\text{Acetochlorhydrine.}} + HCl = \underbrace{\left.\begin{matrix}(C_3H_5)'''\\ C_2H_3O\end{matrix}\right\} O,Cl_2}_{\text{Acetodichlorhydrine.}} + H_2O$$

Acetochlorhydrine and acetodichlorhydrine are neutral liquids, volatile without decomposition.

The action of chloride of acetyle on a mixture of glycerine and acetic acid, produces diacetochlorhydrine.

* Ann. Ch. Phys. (3), lii, 433; Liebig's Jahresbericht (1857), 476.

$$\underbrace{\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\Big\}O_3}_{\text{Glycerine.}} + \underbrace{C_2H_3O,Cl}_{\text{Chloride of acetyle.}} + \underbrace{\begin{matrix}C_2H_3O\\H\end{matrix}\Big\}O}_{\text{Acetic acid.}}$$

$$= \underbrace{\begin{matrix}(C_3H_5)'''\\C_2H_3O\\C_2H_3O\end{matrix}\Big\}O_2,Cl}_{\text{Diacetochlorhydrine.}} + 2\,H_2O$$

If a mixture of equivalent quantities of chloride and bromide of acetyle be allowed to act on glycerine, acetochlorhydrobromhydrine is formed.

$$\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\Big\}O_3 + C_2H_3O,Cl + C_2H_3O,Br$$

$$= \begin{matrix}(C_3H_5)'''\\C_2H_3O\end{matrix}\Big\}O,Cl,Br + \begin{matrix}C_2H_3O\\H\end{matrix}\Big\}O + H_2O$$

Glycerine, in contact with hydrochloric acid and benzoic acid, produces benzochlorhydrine.

$$\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\Big\}O_3 + \underbrace{\begin{matrix}C_7H_5O\\H\end{matrix}\Big\}O}_{\text{Benzoic acid.}} + HCl$$

$$= \underbrace{\begin{matrix}(C_3H_5)'''\\C_7H_5O\\H\end{matrix}\Big\}O_2Cl}_{\text{Benzochlorhydrine.}} + 2\,H_2O$$

Diacetochlorhydrine and acetochlorhydrobromhydrine are neutral liquids, volatile without decomposition.

The majority of the compounds, enumerated under 3, 5, 6, and 8, may be considered to be formed according to the subjoined equation,

$$\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\Big\}O_3 + n\,A - n\,H_2O = B$$

where n is equal to 1, 2, or 3, A stands for one atom of monatomic acid, and B denotes the compound formed.

The formation of trichlorhydrine may be taken as an example.

$$\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\Big\}O_3 + 3\,HCl - 3\,H_2O = (C_3H_5)''',Cl_3$$

Nevertheless there are some compounds which are not formed in accordance with this equation, as exemplified in epidichlorhydrine.

$$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3 + 2\,HCl - 3\,H_2O = (C_3H_4)''Cl_2$$

Epidichlorhydrine.

Epidichlorhydrine is able, nevertheless, if treated with moist oxide of silver, to regenerate glycerine.

In most cases, if hydrochloric acid or the chlorides or bromides of phosphorus act on glycerine, the elements of peroxide of hydrogen separate from the latter, and for HO, one atom of chlorine or bromine enters the compound; but if oxygen acids, such as acetic acid, act on glycerine, the latter exchanges HO for the peroxides of the acid radicals, discovered by Mr. Brodie.

$$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3 - HO + Cl = \left.\begin{matrix}(C_3H_5)'''\\H_2\end{matrix}\right\}O_2,Cl$$

Monochlorhydrine.

$$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3 - 2HO + 2Cl = \left.\begin{matrix}(C_3H_5)'''\\H\end{matrix}\right\}O,Cl_2$$

Dichlorhydrine.

$$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3 - 3HO + 3Cl = (C_3H_5)'''Cl_3$$

Trichlorhydrine.

$$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3 - HO + C_2H_3O_2 = \left.\begin{matrix}(C_3H_5)'''\\H_2\end{matrix}\right\}O_2,C_2H_3O_2$$

Acetine.

The formula of glycerine may therefore be written

$$(C_3H_5)''' \,.\, HO \,.\, HO \,.\, HO$$

and expressions for its derivatives obtained by substituting for HO, either bromine, chlorine, or one of the peroxides of the acid radicals. This mode of representation has been adopted in the following list, which contains the compounds mentioned under 3, 5, 6, and 8. But I wish it to be understood that I do not mean to say that peroxide of hydrogen preexists in glycerine, but merely that in certain reactions the elements HO are exchanged for chlorine, bromine, or compound bodies.

$(C_3H_5)'''(HO)$	(HO)	(HO)	Glycerine.
$(C_3H_5)'''(HO)$	(HO)	Cl	Monochlorhydrine.
$(C_3H_5)'''(HO)$	(HO)	Br	Monobromhydrine.
$(C_3H_5)'''(HO)$	Cl	Cl	Dichlorhydrine.
$(C_3H_5)'''(HO)$	Br	Br	Dibromhydrine.
$(C_3H_5)'''$ Cl	Cl	Cl	Trichlorhydrine.
$(C_3H_5)'''$ Br	Br	Br	Tribromhydrine.
$(C_3H_5)'''$ Br	Cl	Cl	Bromhydrodichlorhydrine.
$(C_3H_5)'''$ Cl	Br	Br	Chlorhydrodibromhydrine.
$(C_3H_5)'''(HO)$	$(C_2H_3O_2)$	Cl	Acetochlorhydrine.
$(C_3H_5)'''(C_2H_3O_2)$	$(C_2H_3O_2)$	Cl	Diacetochlorhydrine.
$(C_3H_5)'''(C_2H_3O_2)$	Cl	Cl	Acetodichlorhydrine.
$(C_3H_5)'''(C_2H_3O_2)$	Br	Cl	Acetochlorhydrobromhydrine.
$(C_3H_5)'''(C_7H_5O_2)$	(HO)	Cl	Benzochlorhydrine.

The following compounds cannot be derived in this manner from glycerine, because their formation does not take place according to the equation mentioned on page 252.

$$(C_3H_5)''' \left\{ \begin{matrix} O'' \\ Br \end{matrix} \right. = (C_3H_4)'' \left\{ \begin{matrix} (HO)' \\ Br \end{matrix} \right. \quad \text{Epibromhydrine}$$

$$(C_3H_5)''' \left\{ \begin{matrix} O'' \\ Cl \end{matrix} \right. = (C_3H_4)'' \left\{ \begin{matrix} (HO)' \\ Cl \end{matrix} \right. \quad \text{Epichlorhydrine}$$

$$(C_3H_4)'' \quad Cl_2 = (C_3H_4)'' \left\{ \begin{matrix} Cl \\ Cl \end{matrix} \right. \quad \text{Epidichlorhydrine.}$$

$C_6H_{11}IO_3$	Iodhydrine.
$C_6H_9BrO_2$	Hemibromhydrine.
$C_3H_7Br_3O$	Compound of dibromhydrine and hydrobromic acid?

9. Glycerine and hydrate of potash form, with evolution of hydrogen, formiate and acetate of potash.*

$$\underbrace{\left.\begin{matrix} C_3H_5 \\ H_3 \end{matrix}\right\} O_3}_{\text{Glycerine.}} + 2 \left\{ \begin{matrix} K \\ H \end{matrix} \right\} O = \underbrace{\left\{ \begin{matrix} C_2H_3O \\ K \end{matrix} \right\} O}_{\text{Acetate of potash.}} + \underbrace{\left\{ \begin{matrix} CHO \\ K \end{matrix} \right\} O}_{\text{Formiate of potash.}}$$

$$+ \quad 4H \quad + \quad H_2O$$

* Dumas and Stass. Ann. Ch. Phys. lxxiii, 148; Ann. Ch. Pharm. xxxiv, 129.

10. A mixture of anhydrous phosphoric acid and glycerine, on being subjected to distillation, yields acroleine.

$$\underbrace{\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3}_{\text{Glycerine.}} - 2H_2O = \underbrace{C_3H_4O}_{\text{Acroleine.}}$$

11. Monochlorhydrine acts on ammonia* and forms the hydrochlorate of a base which Berthelot calls glyceramine.

$$\underbrace{C_3H_7O_2,Cl}_{\text{Monochlorhydrine.}} + N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. = \underbrace{N\left\{\begin{matrix}C_3H_7O_2\\H\\H\end{matrix}\right.}_{\text{Hydrochlorate of glyceramine.}} + HCl$$

According to Berthelot, if a stream of ammonia gas be passed through a solution of dibromhydrine in anhydrous alcohol, bromide of glyceramine is formed. The production of the latter from ammonia and dibromhydrine is intelligible only when we assume that one atom of water takes part in the reaction.

$$\underbrace{C_3H_6O,Br_2}_{\text{Dibromhydrine.}^1} + H_2O + 2NH_3 = \underbrace{N\left\{\begin{matrix}C_3H_7O_2\\H\\H\end{matrix}\right.}_{\text{Hydrobromate of glyceramine.}} + HBr + NH_4Br$$

Tribromide of allyle† acts easily on ammonia, and forms a base called dibromallylamine.‡

$$\underbrace{C_3H_5,Br_3}_{\text{Tribromide of allyle.}} + NH_3 = C_3H_4Br_2 + NH_4Br$$

and—

$$2\left(\begin{matrix}C_3H_4\\Br\end{matrix}\right)',Br + 3NH_3 = \underbrace{N\left\{\begin{matrix}\left(\begin{matrix}C_3H_4\\Br\end{matrix}\right)'\\\left(\begin{matrix}C_3H_4\\Br\end{matrix}\right)'\\H\end{matrix}\right.}_{\text{Dibromallylamine.}} + 2NH_4Br$$

In this instance two atoms of the monobrominated radical allyle replace two atoms of hydrogen in ammonia and form the base in question. The presence of another atom of hydrogen in

* Ann. Ch. Pharm. ci, 76.
† Ann. Ch. Pharm. civ, 247.
‡ Phil. Mag. [4], xvi, 257; Ann. Ch. Pharm. cix, 362.

the latter, replaceable by other radicals, was proved by treating dibromallylamine with iodide of ethyl; ethyldibromallylamine was thus obtained.

$$N\left\{\begin{matrix}(C_3H_4)'\\ Br\end{matrix}\right.\left.\begin{matrix}(C_3H_4)'\\ Br\\ H\end{matrix}\right\} + C_2H_5I = N\left\{\begin{matrix}(C_3H_4)'\\ Br\end{matrix}\right.\left.\begin{matrix}(C_3H_4)'\\ Br\\ (C_2H_5)'\end{matrix}\right\} + HI$$

By treating glycerine with liquid bromide of phosphorus, Berthelot obtained a substance* of the composition $C_6H_9Br_2P$. If in this formula the phosphorus be replaced by nitrogen, we have the formula of dibromallylamine. It is probable that these two substances have a similar constitution, and are related to each other as triethylamine is to triethylphosphine.

12. Nitric acid oxidizes glycerine with great ease, the result of the reaction being an acid called glyceric acid.†

$$\underset{\text{Glycerine.}}{C_3H_8O_3} + O_2 = \underset{\text{Glyceric acid.}}{C_3H_6O_4} + H_2O$$

Glyceric acid is formed from glycerine, in a manner analogous to that of acetic acid from alcohol, or glycolic acid from glycol; two atoms of the hydrogen of the alcohol being replaced by one of oxygen. The acid, which stands to glyceric acid in the same relation as oxalic does to glycolic acid, or malonic‡ to lactic acid, appears to be the tartronic acid of Dessaignes.§

$C_2H_4O_3$	$C_3H_6O_3$	$C_3H_6O_4$
Glycolic acid.	Lactic acid.	Glyceric acid.
$C_2H_2O_4$	$C_3H_4O_4$	$C_3H_4O_5$
Oxalic acid.	Malonic acid.	Tartronic acid.

Although the formation of tartronic acid from glyceric acid has not yet been experimentally established, other properties point out the existence of an intimate connexion between these two substances.

The oxidation of propylo-glycol yields, according to the conditions of the experiment, lactic or glycolic acid.‖

* Ann. Ch. Pharm. ci, 73.

† Phil. Mag., March, 1858; Ann. Ch. Pharm. cvi, 81.

‡ Ann. Ch. Pharm. cvii, 251.

§ Compt. rend. xxxiv, 731; Ann. Ch. Pharm. lxxxii, 362; lxxxix, 339; Jahresbericht (1852), 475.

‖ Ann. Ch. Pharm. cv, 204-5.

$$\left.\begin{matrix}(C_3H_6)''\\ H_2\end{matrix}\right\} O_2 + 2O = \underset{\text{Lactic acid.}}{C_3H_6O_3} + H_2O$$

$$\left.\begin{matrix}(C_3H_6)''\\ H_2\end{matrix}\right\} O_2 + 5O = \underset{\text{Glycolic acid.}}{C_2H_4O_3} + CO_2 + 2H_2O$$

Glyceric acid may be converted into lactic acid,* and tartronic into glycolic acid. The transformations of glyceric and tartronic acids, and their composition, support the view, therefore, that they are connected in the same manner as oxalic and glycolic acids.

According to our knowledge of several salts of glyceric acid, this substance appears to be monatomic. But if we consider its derivation from glycerine, the view of M. Wurtz,† who considers glyceric acid to be triatomic, is very probably correct.

$$\left.\begin{matrix}(C_3H_3O)''\\ H_3\end{matrix}\right\} O_3 \quad \text{Glyceric acid.}$$

This point, however, requires further investigation.

Thus by a variety of reactions, we recognize glycerine to be derived from three atoms of water, and to contain three atoms of hydrogen, replaceable by other radicals and the triatomic radical (C_3H_5). Accordingly we obtain from glycerine and a monatomic acid, at least three compounds, corresponding to the ethers of common alcohol, and with hydrochloric acid at least three chlorides, the formation of which takes place in a manner analogous to that of chloride of ethyl from $\left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\} O$, or of chloride of potassium from $\left.\begin{matrix}K\\ H\end{matrix}\right\} O$. The same reaction, which occurs *once* in these two instances, repeats itself in the case of glycerine *three* successive times. The great number of compounds, which can be prepared in this way by changing the acids, may be considerably augmented by employing two or three different acids at the same time, as illustrated by the following examples.

$(C_3H_5)'''$	(HO)	(HO)	(HO)	Glycerine.
$(C_3H_5)'''$	(HO)	$(C_2H_3O_2)$	Cl	Acetochlorhydrine.
$(C_3H_5)'''$	Br	$(C_2H_3O_2)$	Cl	Acetochlorhydrobromhydrine.

* Ann. Pharm. cix, 227; Phil. Mag., December, 1858.

† Société Chimique de Paris (13 Mai, 1859), 38.

But the triatomic radical C_3H_5, by a modification in its constitution, connects the glycerine series with other interesting compounds. Under the influence of iodide of phosphorus, iodide of allyle is formed from glycerine, in which the radical C_3H_5 is monatomic. From iodide of allyle, allylic alcohol and its derivatives can be prepared as well as glycerine be regenerated. Acroleine, the aldehyde of allylic alcohol, may also be produced by the direct action of phosphoric acid on glycerine. Iodide of allyle, hydrochloric acid and mercury generate propylene; and the dibromide of the latter enables us to prepare propylo-glycol and its derivatives, including lactic acid. If sulphuric acid, which has been allowed to absorb propylene, be distilled with water, propylic alcohol is obtained, and the preparation of the numerous bodies of the propylic series becomes practicable. Thus we find propylic alcohol, propylo-glycol, allylic alcohol and glycerine, and their respective derivatives, intimately connected.

(C_3H_5), monatomic in . . . . . $\underset{\text{H}}{(C_3H_5)'}\Big\}O$

Allylic alcohol.

$(C_3H_5)'''$, triatomic in . . . . . $\underset{\text{H}_3}{(C_3H_5)'''}\Big\}O_3$

Glycerine.

$(C_3H_5)''',H$ . . = $(C_3H_6)''$, diatomic in . $\underset{\text{H}_2}{(C_3H_6)''}\Big\}O_2$.

Propylo-glycol.

$(C_3H_5)''',HH$. = $(C_3H_7)'$, monatomic in . $\underset{\text{H}}{(C_3H_7)'}\Big\}O$

Propylic alcohol.

XXII.—*Action of Metals upon Iodide of Ethylene* $C_4H_4I_2$.

By Carl Von Than and J. A. Wanklyn.

When zinc acts upon iodide of ethyl, it combines both with the iodine and with the ethyl, producing iodide of zinc and zinc-ethyl.

In like manner it seemed possible that zinc would act upon iodide of ethylene in such a manner as to give iodide of zinc and a compound of zinc with the biatomic radical ethylene, thus :—

$$(C_4H_4)''I_2 + Zn_4 = (C_4H_4)''Zn_2 + Zn_2I_2$$

We have tried the experiment, using ether to dissolve the iodide of ethylene, and obtained a negative answer as regards the production of a compound of the biatomic ethylene with zinc.

Our research was conducted as follows :—The iodide of ethylene was prepared by passing olefiant gas over iodine gently warmed with hot water. The product was freed from excess of iodine by means of a solution of caustic potash, washed and dried by pressure between folds of bibulous paper; afterwards it was exposed for a short time in vacuo over sulphuric acid. The ether was dried by standing over solid caustic potash. The zinc was pretty pure and finely granulated.

A few grammes of this iodide of ethylene were introduced into a glass tube along with zinc and ether, and hermetically sealed therein before the blowpipe. The tube so prepared was kept at ordinary temperatures and in the dark. Large quantities of a combustible gas were gradually evolved. This gas was allowed to escape from time to time by opening the tube; and some of it was collected over water, transferred to the mercurial trough and analysed, when it proved to be perfectly pure olefiant gas, as the following particulars of the analysis show :—

	Volume.	Pressure, in Metres.	Temperature Centigrade	Volume at 1 metre and 0°C.
Volume of gas taken	83·5	0·1483	17·8°	11·61
After the addition of oxygen	467·6	0·5272	17·7°	231·5
After the explosion	440·8	0·5022	17·5°	208·1
After the absorption of carbonic acid ..	409·8	0·4860	20·9°	185·0

	Found	Calculated for C_4H_4
Volume taken . .	11·61	11·62
Contraction . . .	23·40	23·24
Carbonic acid . .	23·10	23·24
Oxygen consumed	34·89	34·86

That the gas was not a mixture, having the same percentage composition and condensation as ethylene, was proved by its complete absorption by fuming sulphuric acid.

The residue in the production tube consisted apparently of nothing beyond iodide of zinc dissolved in ether. Some of the contents were withdrawn and treated with water, with which they did not effervesce; the rest were distilled directly from the production tube, a cork and bent tube having been previously adapted thereto. This distillation was commenced in the water bath, and finished over the naked flame. No product containing zinc distilled over. No compound of ethylene and zinc seems, therefore, to be formed by this process, and the reaction which actually takes place may be thus written:—

$$(C_4H_4)''I_2 + Zn_2 = C_4''H_4 + Zn_2I_2$$

With other metals we have obtained similar results.

Sodium with ethereal solution of iodide of ethylene evolves gas rapidly at ordinary temperatures. This gas was evidently ethylene, as it was soluble in fuming sulphuric acid, after it had been free from ether vapour by washing with water. The iodide of sodium which formed simultaneously with the gas, was coloured blue. A blue coloration of iodide of sodium had been previously remarked by one of us when iodide of ethyl, ether, and sodium, are brought together.

Mercury also evolves gas when placed in an ethereal solution of iodide of ethylene. In that case, the evolution takes place slowly; but ultimately an immense quantity of gas is given off, even when the experiment is conducted at ordinary temperatures, and with exclusion of light. At the same time, iodide of mercury makes its appearance and gradually assumes the red modification. No signs of any combination between ethylene and mercury were observable.

We have also extended our experiments to chloride of ethylene $(C_4H_4)''Cl_2$ (Dutch liquid). This liquid mixed with dry ether is not acted upon by zinc, either at ordinary temperatures or in the water bath. By sodium, however, it is attacked when gently warmed, even though the heating falls considerably short of 100°C. Olefiant gas and blue chloride of sodium are the products. The gas was collected over water, and subsequently treated with strong sulphuric acid, by which it was perfectly absorbed, proving the entire absence of free hydrogen.

The reactions established in this paper are of interest in relation to the theory of biatomic radicals, and may be regarded as cases in which the biatomic radical ethylene is isolated. Just as under certain conditions, iodide of ethyl yields ethyl when acted upon by zinc, so does iodide of ethylene yield ethylene when treated with that metal. The parallelism between the following equations is obvious:—

$$2(C_4H_5I) + Zn_2 = Zn_2I_2 + \left.\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right\}$$

$$(C_4H_4)''I_2 + Zn_2 = Zn_2I_2 + C_4''H_4$$

It is our intention to seek for metallic combinations of the biatomic radical ethylene by the employment of other methods than the one mentioned in this paper.

XXIII.—*Researches on the Atomic Weight of Graphite.*

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[For the numbers of the analyses given in this communication, and for other details, see the author's paper on the Atomic Weight of Graphite in the current number of the Philosophical Transactions.]

The following research was undertaken with the hope of throwing light upon a very obscure problem, the nature of the allotropic conditions of the elemental bodies. My object was to ascertain whether this difference of condition was to be regarded as a purely physical, or as a chemical difference of matter. If it were a chemical difference, then different allotropic forms must exhibit different chemical reactions, and it was to be anticipated as not improbable that these different forms might even enter into combination with different combining weights. No fact of this nature has yet been ascertained; but among the physical properties of the allotropic forms of the elements, there was one which will hereafter be referred to, by which this result was indicated. In the great majority of cases the allotropic conditions of an element are

so easily convertible, and have so little permanence that we could hardly hope to discover any chemical difference between them, even if such exists. Certain instances, however, may be found of more permanent forms; of which the most remarkable is that of the forms of carbon. The forms of carbon are identified by the fact that by combustion in oxygen they can all be converted into one and the same substance, carbonic acid; but this transformation requires great heat; and within a very considerable range of temperature, the forms of carbon are unaffected by those causes which in other cases determine the transition of the allotropic forms of an element into its one most permanent state. I therefore examined with care the chemical reactions of carbon.

Some account of that remarkable substance which afforded the material of this inquiry may not be without interest. The term graphite has been applied indiscriminately to several varieties of native carbon, which have but little in common. Among these, however, two may be especially distinguished by their superior brilliancy and by their metallic streak. The one of these varieties possesses a distinct lamellar structure and the lustre of a metal; in appearance it resembles molybdenum; the other is amorphous, and appears as a powder of a silver-grey colour. The lamellar graphite is imported into this country chiefly from Ceylon, where it is found in large masses associated with quartz. It exists also in many other localities; at Travancore, and in Spain, and in small quantities is frequently discovered, associated with volcanic minerals.

The amorphous graphite is now chiefly procured from Germany; I believe from Passau, in Bavaria. Formerly mines of it existed at Borrowdale, in Cumberland, but these are nearly exhausted. It is of much less frequent occurrence than the other kind. In the following investigation, the term graphite is limited to these two varieties. The lamellar graphite is also formed artificially during the process of iron smelting, when it is dissolved by, and combines with, the iron. On dissolving cast iron in an acid, a residue is left of from 3 to 4 per cent. of graphite. I know of but one example of the artificial formation of amorphous graphite; the carbon which is deposited on the electrode during the passage of the electric light, is in this condition. This carbon is soft, amorphous, and has the streak of a fine black-lead pencil. This change is doubtless effected by the intense heat, the extremities of both poles being in the same condition. Of the other varieties of

native carbon, which have been vaguely termed graphite, at least two exist in large deposits. A deposit of carbon is found in New Brunswick, very similar in appearance to anthracite coal. In Greenland also there is a large deposit of carbon which is in its properties intermediate between this and the true graphite.

Several applications have been made of graphite in the useful arts. Mixed with clay it is employed in the manufacture of the crucibles used in gold refining. It is also extensively used for the glazing of certain varieties of gunpowder, specially that employed for blasting. The graphite is finely ground, and the gunpowder rolled with it in iron cylinders. It is also used for the protection of iron from rust, and, mixed with grease, for the lubrication of machinery. Its most important application is for the manufacture of pencils. For this purpose it is consolidated by pressure into blocks, from which the pencil is afterwards cut, or it is mixed with an aggregating material, made into a paste, and moulded into the required form. The ingenious process of the late Mr. Brockedon for the compression of black lead for pencils is well known.

The first experiment in which I succeeded in eliciting a difference in the chemical reactions of the different forms of carbon was in the action upon them of a mixture of concentrated nitric and sulphuric acids. When finely-divided carbon, in the form of lamp-black, or charcoal from the decomposition of sugar, is heated with a mixture of 1 of nitric and 4 of sulphuric acids, the carbon is rapidly oxidized, and a black substance is formed soluble in the concentrated acid, but precipitated on the addition of water. This substance is insoluble in acids and saline solutions, but is soluble in pure water and in alkalies. It is accompanied with other products which render its purification difficult. When the graphite of Ceylon is treated in a similar manner, the result is very different; the graphite becomes of a beautiful purple colour, and falls to pieces in the fluid. The substance, after the acid has been washed from it by water, has much the appearance of the graphite itself, but is darker in colour. It was found on analysis to contain the elements of sulphuric acid combined with oxygen, with hydrogen, and with a large amount of carbon. My efforts to procure this substance of a constant composition have been unavailing; it is insoluble in all reagents; it may be boiled with a strong solution of potash without separation of sulphuric acid, and with slight, if any, alteration of weight. When heated, it

undergoes a remarkable change; gases are given off in the interior of the substance, which swells up in a singular manner, and is reduced to the minutest state of division. The residue consists of carbon which has the appearance and the structure of the lamellar graphite. This decomposition may be compared in its appearance with that which the chromate of ammonia undergoes by the action of heat.

The experiment may be applied to the disintegration and purification of graphite for purposes of the arts, with which view the process has been patented. Its details are as follows: One pound of powdered graphite is mixed with 4 pounds of concentrated sulphuric acid, with this is mixed 1 ounce of powdered chlorate of potash. The mixture is heated until chlorous fumes cease to be evolved; the residue is thrown into water, washed out, dried, and ignited. The ignited substance is washed in water, in which it floats, while the impurities fall to the bottom. It is then dried. By this process graphite may be obtained in a state of chemical purity.

These experiments established a point of considerable importance: the existence of a peculiar compound of carbon in the form of graphite. Its discovery led me to turn my attention to the oxidation of graphite. I found that graphite, heated with a mixture of nitric acid and chlorate of potash, increased in weight, and that the substance formed was, on the application of heat, disintegrated with evolution of gas. The disintegrated substance differed but little in appearance from the original graphite. I found, however, that when the substance formed by the treatment of graphite with the oxidizing mixture was washed free from the salts produced in the reaction, dried at 100°, and again oxidized, it gradually underwent a change in appearance, until after the fourth and fifth repetition of the process, the whole of the graphite was converted into a substance of a light yellow colour, consisting of minute, transparent, and brilliant plates. Analysis further showed that this change was attended with a gradual alteration of the constitution of the substance, but that finally a time arrived when further treatments with the oxidizing mixture produced no further change. It is remarkable that this change cannot be produced by one prolonged treatment; before the oxidation can proceed, the original conditions must be restored.

The details of this process are as follows:—A portion of graphite

is intimately mixed with three times its weight of chlorate of potash, and the mixture placed in a retort. A sufficient quantity of the strongest fuming nitric acid is added, to render the whole fluid. The retort is placed in a water-bath, and kept for three or four days at a temperature of 60° C. until yellow vapours cease to be evolved. The substance is then thrown into a large quantity of water, and washed by decantation nearly free from acid and salts. It is then dried in a water-bath, and the oxidizing operation repeated with the same proportion of nitric acid and of chlorate of potash until no further change is observed; this is usually after the fourth time of oxidation. The substance is ultimately dried, first in vacuo and then at 100°. A modification of the process which may be advantageously adopted, consists in placing the substance with the oxidizing mixture in flasks exposed to sunlight. Under these circumstances the change takes place more rapidly, and without the application of heat.

The analysis of this substance, when the necessary correction is made for the residual ash, gave the following numbers, the mean of nine concordant determinations.

Carbon . . .	61·04
Hydrogen . .	1·85
Oxygen . . .	37·11
	100·00

These numbers correspond with the formula $C_{11}H_4O_5$ (C = 12) which requires

C_{11} . .	132	61·11
H_4 . .	4	1·85
O_5 . .	80	37·04
	216	100·00

The crystals of this substance were ascertained by Professor Miller, of Cambridge, to belong either to the prismatic or the oblique system. It is insoluble in water containing acids or salts, but is very slightly soluble in pure water. It combines with alkalies and the crystals have an acid reaction. Agitated with dilute ammonia, it is converted into a transparent jelly, but the substance is not dissolved. On the addition of acids, it is separated unaltered from this combination, as a gelatinous mass

resembling silica. Treated with deoxidizing agents, it is readily decomposed. When a solution of sulphide of ammonium or of potassium is poured upon the dry substance, a crackling sound is heard, and a body is ultimately formed possessing the metallic lustre and general appearance of graphite itself. Changes similar in appearance take place on boiling the substance with an acid solution of protochloride of copper and of protochloride of tin.

The crystals on the application of heat are decomposed with ignition; gases are evolved, and a black residue is left of a body resembling in appearance finely-divided carbon. I propose for this substance the name, *Graphic acid.*

I have in vain attempted to procure the product of the decomposition by heat of the graphic acid, until it occurred to me to effect the decomposition in a fluid medium by which the particles of the substance were separated from one another and elevation of temperature precluded. The fluid which I selected for the experiment was the mixture of hydrocarbons of high boiling points from the Rangoon naphtha. When graphic acid is heated in this fluid to a temperature of about 270°, water is given off, and a brisk evolution ensues of carbonic acid, the hydrocarbon at the same time becoming of a deep red colour. The residual substance resembles graphite, and gave as the mean of several analyses, the following numbers

Carbon . . .	80·13
Hydrogen . .	0·58
Oxygen . . .	19·29
	100·00

which correspond with the formula $C_{22}H_2O_4$.

C_{22} . .	264	80·00
H_2 . .	2	0·60
O_4 . .	64	19·40
	330	100·00

When this substance is heated in a current of nitrogen to a temperature of 250°, a further change ensues; water is given off

accompanied by a small quantity of carbonic oxide. An analysis of the resulting substance gave the following numbers

Carbon . . .	81·80
Hydrogen . .	0·44
Oxygen . . .	17·76
	100·00

which corresponds with the formula $C_{66}H_4O_{11}$ which requires

C_{66} . .	792	81·48
H_4 . .	4	0·41
O_{11} . .	176	18·11
	972	100·00

This substance would be derived from the preceding by the elimination of 1 atom of water from 3 atoms of the original substance. On a greater elevation of temperature, carbonic acid, carbonic oxide, and water are again evolved, but the body may be exposed to a red heat for several hours in a current of nitrogen, and only undergo a very partial decomposition, the residual substance still containing a considerable portion both of hydrogen and oxygen.

Buff and Wöhler have recently discovered a remarkable series of compounds derived from the graphitoidal form of silicon,* among which is a compound of silicon, hydrogen, and oxygen, of the formula $Si_4H_4O_5$. The general properties of this substance correspond very closely with those of the graphite compound, as separated from its combinations by an acid. It is described as a white and voluminous body which floats upon water, in which it is very slightly soluble. We may therefore reasonably infer, that the graphite-compound is the same term in the system of carbon, as the silicon-compound in the system of silicon. When we proceed to state this analogy in the formula of the substance, we are led to very remarkable conclusions.

The total weight of graphite, which in the compound is combined with 4 atoms of hydrogen and 5 of oxygen, is 132. If we assume that this weight is, like the corresponding weight, 84 of silicon, to be divided into 4 parts, we arrive at the number 33, as the atomic

* Ann. Ch. Pharm. vol. civ. p. 94.

weight of graphite. Representing this weight by the letters Gr., the formulæ of the substances $C_{11}H_4O_5$, $C_{22}H_2O_4$ and $C_{66}H_4O_{11}$ become $Gr_4H_4O_5$, $Gr_8H_2O_4$ and $Gr_{24}H_4O_{11}$.

There is a property of graphite by which these formulæ may be tested.

According to the law of Dulong and Petit, the specific heats of the elemental bodies vary inversely with their atomic weights. The elements are divided into two classes, the one in which the product of the specific heat into the atomic weight is approximately 3·3, the other in which this product is approximately 6·6. This law expresses the only common physical property by which these weights are characterized. The specific heat of carbon however presents a remarkable exception to it. It differs in the different allotropic forms of carbon. The specific heat of native graphite as determined by Regnault is 0·20187. Now $6 \times 0{\cdot}201 = 1{\cdot}206$ and $12 \times 0{\cdot}201 = 2{\cdot}412$, which are not within the limits of error. But if we assume the atomic weight of graphite as 33, we have for the products of the specific heat into the atomic weight, the number 6·6 which is according to the law, this product being the same as the product of the specific heats into the atomic weights of the elements phosphorus, antimony, arsenic, bismuth, and iodine.

The relation also which exists between the atomic weights of boron, silicon, and zircon, and that form of carbon for which a place may be claimed as a distinct element, *graphon*, is precisely the kind of numerical relation which is found to exist between the weights of analogous elements. We have

Boron . . .	11
Silicon . . .	21
Graphon . . .	33
Zircon . . .	66

These considerations lead to the remarkable inference that carbon in the form of graphite functions as a distinct element, that it forms a distinct system of combinations into which it enters with a distinct atomic weight, the weight 33. Analogy would lead us to a similar conclusion with regard to the elements boron and silicon. How far this inference is to be extended to the allotropic forms of other elements, experiment alone can decide.

XXIV.—*On the Combination of Carbonic Oxide with Potassium.*

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It is now some years since Liebig made the curious observation that carbonic oxide is absorbed by and combines with potassium. This distinguished chemist did not make any exact experiment on the amount of this absorption, and simply put forward a conjecture upon the subject founded upon the inadequate data in his possession. From that time to the present, the reaction has not been further investigated. It appeared to me that, viewed in connection with recent experiments, this question assumed a new interest, and that it was probable that the reaction was of a much simpler character than Liebig had surmised. In the more close examination of this experiment, I have discovered some remarkable points in it, which have not hitherto been observed.

The carbonic oxide used in the follwing experiments was prepared by the process of Fownes, the decomposition of ferrocyanide of potassium, by concentrated sulphuric acid; the gas was carefully dried and purified, any traces of oxygen from air accidentally present being separated by the passage of the gas through a Liebig's apparatus containing pyrogallate of potash. The potassium also was, as far as possible, freed from adhering impurities by filtration through wash-leather immediately before the experiment. This purification of the potassium, so that it shall present a perfectly clean surface to the action of the gas, is an essential condition of success. The potassium was rapidly wiped from naphtha by blotting paper and introduced into a bulb tube, or, when large quantities were operated on, into a Florence flask, which had previously been filled with carbonic oxide and weighed. The vessel containing the potassium was heated in an air bath in such a manner that the progress of the experiment could be observed. A gage-tube dipping into mercury was attached to the apparatus, which was rendered air tight. The absorption commences considerably under 100°C., and at about 80°C. a change in the potassium is indicated by the appearance of the most beautiful arborescence, the potassium shooting out into crystals resembling

frosted silver in appearance, and at the same time spreading itself over the surface of the glass. This change continues until the whole of the potassium has become similar in appearance, and converted into these crystals of a dead grey colour. The metallic appearance which the crystals at first present is most probably due to the spreading out of the metal over the surface. During this change, the gauge-tube indicates a slow and moderate absorption, the mercury standing at the level of about half an inch in the tube, while the passage of the gas is regulated with extreme slowness. If pressure is put on the gas so as to accelerate its passage, it bubbles through the apparatus. The formation of this substance is the first stage in the action. On its completion, a further change is indicated by the formation of dark spots on the surface of the crystals, which, when their formation has once commenced, spread over the surface with great rapidity, the carbonic oxide being simultaneously absorbed. This absorption is as rapid as the absorption of carbonic acid by potash, and if the gas be not allowed sufficiently free access to the substance, the mercury will indicate in the guage tube a pressure of from 20 to 30 inches. It is attended with great evolution of heat. This absorption takes place with the greatest rapidity at comparatively low temperatures. With the aim of preserving the substance in this stage, I have frequently allowed the temperature to fall before the formation of the dark spots indicated the further alteration. At a certain stage however in the cooling, when the temperature has perhaps fallen as low as 40°C., the second action almost invariably commences nor have my efforts to procure this body in a pure condition by means of other devices been more successful. The final product of the experiment is of a dark red colour and retains the crystalline form of the body from which it is produced. During the progress of the experiment, spots of blue and green appear on the substance indicating the partial formation of other bodies. The constitution of the substance is determined by the following experiments:—

Potassium taken.	Increase in weight.	Increase in weight on 100 parts.
6·40 grms.	4·57 grms.	71·4
5·461 „	3·967 „	72·4
0·674 „	0·475 „	70·48
4·858 „	3·469 „	71·4
5·6886 „	4·086 „	71·8
4·669 „	3·362 „	72·07

In these six experiments, which I have selected at random from a larger number giving equally concordant results, the mean increase in weight on 100 parts of the substance is 71·59 parts, and 100 parts of the sustance formed are thus constituted.

Potassium . . .	58·27
Carbonic oxide . . ,	41·73
	100·00

On the assumption that one atom of potassium weighing 39·2 absorbs 1 atom of carbonic oxide weighing 28, 100 parts of potassium would absorb 71·2 parts of carbonic oxide, and the constitution of the substance formed would be—

K	39·2	58·33
CO	28.0	41·67
	67·2	100·00

The experiments of Berthelot have shewn that carbonic oxide combines with hydrate of potash to form formiate of potash, formic acid that is, in which one atom of hydrogen is replaced by one of potassium Now the result of this experiment, the body COK (or rather $C_2O_2K_2$) has the constitution of the radicle of formic acid, $C_2O_2H_2$, in which the whole of the hydrogen is replaced by potassium. It is not improbable that the intermediate substance may be the body COK_2, or the hydride of formyle, in which a similar replacement is effected.

Experiments which I have made with the view of replacing the potassium in this substance by organic groups have been without result. Neither iodide of ethyl nor even chloride of benzoyl act upon it, There is every reason to believe that it consists of two bodies, anhydrous potash, and rhodizonate of potash. Brought in contact with water, it decomposes with terrific violence, and even the dry substance, under circumstances which are not well ascertained, occasionally explodes. It may be preserved under naphtha. When pure and anhydrous alcohol is poured upon it, a great elevation of temperature ensues but the decomposition is far less violent than with water. Even this experiment, however, must be made with the greatest caution. No gas is given off, but a

portion of ethylate of potash remains in solution, and the rhodizonate appears as a red insoluble powder. I endeavoured to ascertain the nature of this decomposition. Alcohol was repeatedly digested with, and poured off from the residue; and the potash was precipitated from it by carbonic acid, and determined as sulphate.

Two experiments gave the following results:—

I. 100 parts of potassium absorbed 72·4 parts of carbonic oxide, and 38·4 parts of potassium were extracted by the alcohol.

II. 100 parts of potassium absorbed 71·8 parts of carbonic oxide and 41·77 parts of potassium were extracted by the alcohol.

We may assume therefore that of 5 parts of the potassium taken, 2 are extracted by the alcohol and 3 remain in the residue as rhodizonate, which would give for its constitution $C_{10}O_8K_6$

$$5C_2O_2K_2 = 2K_2O + C_{10}O_8K_6$$

I do not pretend that the constitution of the rhodizonate can be thus determined with certainty, but its formula has never yet been ascertained by any adequate and reliable experiments. Such efforts as I have made to ascertain it have been defeated by the extreme facility with which it is oxidized with formation of croconate. Rhodizonate of potash if perfectly pure, dissolves in dilute acetic acid with a pale pink colour, and the solution gives with acetate of baryta a brilliant red precipitate; but this precipitate alters in colour during the process of washing, and the solution of the potash-salt speedily becomes alkaline and yellow from the formation of croconate. I have never seen the oxalate of potash which others have observed in the decompositions of this class of bodies; and I may observe that this decomposition, with the formation of croconate of potash and hydrate of potash, can readily be accounted for on the hypothesis I have given, simply by the action of air and moisture.

$$C_{10}O_8K_6 + H_2O + O_3 = 2(C_5O_5K_2) + 2(KHO)$$

Croconate of Potash